On-shore and off-shore tephrostratigraphy: Mass budgets, Time series, and Implications for geological processes

Habilitationsschrift
vorgelegt bei der
Mathematisch-Naturwissenschaftlichen Fakultät
der Christian-Albrechts-Universität zu Kiel

von
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Kiel, 2013

Preface

The seven manuscripts presented in the appendix are linked around the general theme of on-shore and off-shore tephrostratigraphy and how other cognate research fields can benefit from this approach. They all focus on the application of marine and on-shore tephra studies to volcanological and geological questions. Two of the manuscripts focus on the development of different tephrostratigrapic frameworks throughout entire on-shore and off-shore regions. The other five manuscripts aim to use tephrostratigraphic fundamentals of different scales to estimate magma fluxes, conduct provenance studies, and determine the timing and cyclicity of geological processes. The entirety of this work is subdivided into two chapters. Chapter 1 provides an overview of tephrostratigraphy and presents its basic concepts, on- and offshore. In chapter 2 the seven manuscripts are presented as case study summaries of major results, and establish bridges between single studies in order to point out the geological benefits of tephrostratigraphy. In sections 2.1 to 2.4 fundamental volcanological questions and tephrostratigraphics methods are addressed using tephras from different locations and settings. The last three sections (2.5. to 2.7.) focus on the application of tephrostratigraphy as a tool for solving broader geological problems.

Section 2.1 (Kutterolf et al. 2007) focuses on the tephrostratigraphy of Late Pleistocene to Holocene highly-explosive eruptions of west-central Nicaragua, and in the reconstruction of their eruptive parameters. Extending this tephrostratigraphic work towards North and South Central America and further into the past is the focus of section 2.2 (Kutterolf et al. 2008a). This Central American tephra study serves as the basic framework for sections 2.3 and 2.5, and incorporates land and marine tephras that have been correlated over long distances. New ages estimated from sedimentation rates complement the age framework for Central American tephras derived from ^{14}C and Ar/Ar datings of on-shore tephras. In section 2.3 (Kutterolf et al. 2008b), the construction of distal isopach maps for each identified marine tephra, together with field data from the literature and own field work, facilitated a more precise and reliable volume and mass estimation of the late Pleistocene to Holocene Plinian eruptions. Converting the erupted tephra volumes to erupted masses and incorporating the effusive volcanic products from the volcano edifices given in literature resulted in a minimum estimate of long-term average magma production rate for each volcano, for different regions, and for the whole Central American volcanic arc. A determination of erupted volumes combined with provenance and sedimentological studies of late Miocene tuffaceous sandstones presented in section 2.4. (Kutterolf et al. sub) is the continuation of this approach in the Shikoku basin, near the Nankai Trough (Japan). This manuscript uses geochemical criteria to constrain the source region of Miocene sandstone beds that are rich in volcanic matter, and assesses volume estimates for their related eruptive events. The application of tephrostratigraphy for slope geology is extensively described in section 2.5. (Kutterolf et al. 2008c) and focuses mainly on the forearc region of Nicaragua and Costa Rica. Using the ages from the tephras and the tephras themselves as marker beds, facilitates the determination of variable sedimentation rates reflecting changes in the regional stress field, as well as the laterally and temporally variable phases of excess sediment delivery and erosion at the slope. Additionally, well-dated tephras within sediments related to submarine landslides, helps to estimate the timing of slope failure initiation at the Nicaraguan slope within the last 60 ka, as well as the long term history of fluid venting in that area. Kutterolf et al. (2008d; section 2.6.) continues this application and combines the marine tephra age framework with radiometric dating of carbonates and with sediment analyses around cold seep vents at the Costa Rican and Nicaraguan slopes to evaluate how these structures evolve in time and space. Finally, section 2.7. (Kutterolf et al. 2013) focuses on the tephrostratigraphic framework of the entire Ring of Fire region to evaluate the amount and cyclicity of larger eruptions within the last million years in terms of the global response of volcanism to climate forcing.

In conclusion, the results obtained in these studies show that the combined tephra record from explosive volcanic eruptions on-shore and offshore facilitates 1) better constrains on erupted ash volumes and their provenance, 2) the establishment of reliable volcanic mass fluxes at subduction zones, 3) the allocation of marker beds to understand fore arc processes, 4) an estimation of variable marine erosion and accumulation rates, and 5) deduction of first order cyclic behavior in the sediment-keeping tephra record, and second order periodical behavior of the underlying geological processes.

I wrote 70-90% of the seven publications that are part of this Habilitationsschrift. My personal contributions can be broken down as follows: for the publication *Kutterolf et al. (2007)* my contribution to the writing and data acquisition was 75% and 60%, respectively. For the papers *Kutterolf et al. (2008a)*, *Kutterolf et al. (2008b)*, and *Kutterolf et al. (2008c)*, I was responsible for about 80% of the writing and 90% of the data acquisition. I wrote 90% of *Kutterolf et al. (sub)* and contributed 80% of the data acquisition. Finally, *Kutterolf et al. (2008d) and Kutterolf et al. (2013)*, were written by me by 70% and data acquisition and processing was done by myself by about 65%.

In addition to the papers specified in this *Habilitationsschrift*, two additional first-author papers and 16 publications, in which I have contributed as a co-author, were published within the last five years. All of these papers, which are listed below, were not part of my dissertation. My personal contributions to the first-author papers Kutterolf et al. (2007, 2011) are about 70% and 80% for writing and data acquisition, respectively. In the co-authored papers my overall participation was less than 30% of manuscript writing and about 50% for data acquisition.

Additional papers not included in this *Habilitationsschrift*:

1) Papers that are not part of my dissertation but related to the Habilitation (last 5 years):

Kutterolf S., Freundt A., Burkert C. (2011), Eruptive history and magmatic evolution of the 1.9 ka Plinian dacitic Chiltepe Tephra from Apoyeque volcano in west-central Nicaragua, Bull Volc., 73, 811-831, doi: 10.1007/s00445-011-0457-0

Kutterolf S., Schacht U., Wehrmann H., Freundt A., Mörz T. (2007b) Onshore to offshore tephrostratigraphy and marine ash layer diagnesis in Central America. In: J. Buntschuh and G.E. Alvarado (eds) Central America - Geology, Resources and Hazards, Taylor & Francis /Balkema, ISBN-13:978-0-415-41648-1: 395-423

Metzner D., **Kutterolf S**., Toohey M., Timmreck C., Niemeier U., Freundt A, Krüger K. (in press) Radiative forcing and climate impact resulting from SO2 injections based on a 200,000 year record of Plinian eruptions along the Central American Volcanic Arc. Int J Earth Sci. doi:10.1007/

Gilbert D., Freundt A., **Kutterolf S.**, Burkert C. (in press) Post-glacial time series of explosive eruptions and associated changes in the magma plumbing system of Lonquimay Volcano, South Central Chile. Int J Earth Sci. doi:10.1007/s00531-012-0796-x

Geilert, S., Freundt, A., Wörner, G., **Kutterolf, S**. (2012) Geochemical differences between along-arc and across-arc volcanics in west-central Nicaragua, J South Am Earth Sci, 35, 38-50.

Voelker D., **Kutterolf S.**, Wehrmann H. (2011) Comparative mass balance of volcanic edifices at the Southern Volcanic Zone of the Andes between 33°S and 46°S, J Volcanol Geotherm Res, 205, 114-129, doi:10.1016/j.jvolgeores.2011.03.011.

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Schacht U., Wallmann K., **Kutterolf S**. (2010) The Influence of Volcanic Ash Alteration on the REE Composition of Marine Pore Waters, J Geochem Exp, 106:176-187, doi:10.1016/j.gexplo.2010.02.006.

Mueller A.D., Anselmetti F.S., Ariztegui D., Brenner M., Curtis J.H., Escobar J., Gilli A., Grzesik D.A., Hodell D.A., Guilderson T.P., **Kutterolf S.**, Plötze M.L .(2010) Late Quaternary Palaeoenvironment of Northern Guatemala: Evidence from Deep Drill Cores and Seismic Stratigraphy of Lake Petén Itzá, Sedimentology, 57/5, 1220-1245, DOI: 10.1111/j.1365-3091.2009.01144.x.

Schmincke H.U., Rausch J., **Kutterolf S.**, Freundt A. (2010) Walking through volcanic mud: the 2,100 year-old Acahualinca footprints (Nicaragua) II: the Acahualinca people, environmental conditions and motivation. Int J Earth Sci, 99, 279-292 doi:10.1007/s00531-009-0438-0.

Harders R., **Kutterolf S.**, Hensen C., Moerz T., Brueckmann W. (2010) Tephra layers: A controlling factor on submarine translational sliding?, Geochem. Geophys. Geosyst., 11, Q05S23, doi:10.1029/2009GC002844.

Schmincke H.-U., **Kutterolf S.**, Perez W., Rausch J., Freundt A., Strauch W., (2009) Walking through volcanic mud: the 2,100-year-old Acahualinca footprints (Nicaragua): Bulletin of Volcanology, v. 71, p. 479-493.

Peréz, W., Freundt A., **Kutterolf S.**, Schmincke H.-U. (2009), The Masaya Triple Layer: a 2100 year old basaltic multi-episodic Plinian eruption from the Masaya Caldera Complex (Nicaragua), J Volcanol Geotherm Res, doi:10.1016/j.jvolgeores.2008.10.015.

Schacht U., **Kutterolf S.**, Bartdorff, O., Corrales Cordero, E. (2009) Pore water composition of volcanogenic sediments from across the Central American Subduction Zone, J Geochem Exp, 101, pp 88, doi: 10.1016/j.gexplo.2008.11.035.

Hodell D.A., Anselmetti F.S., Ariztegui D., Brenner M., Curtis J.H., Escobar J., Gilli A., Grzesik D.A., Guilderson T.J., Müller A.D., Bush M.B., Correa-Metrio A., Escobar J., and **Kutterolf S**. (2008) An 85-ka Record of Climate Change in Lowland Central America. Quart Sci Rev, doi:10.1016/j.quascirev.2008.02.008.

Wallmann K., Aloisi G., Tishchenko P., Pavlova G., Häckel M., Greinert J., **Kutterolf S.**, Eisenhauer A. (2008) Silicate weathering in anoxic marine sediments. Geochim Cosmochim Acta, doi:10.1016/j.gca.2008.03.026.

Schacht U., Wallmann K., **Kutterolf S.**, and Schmidt M. (2008) Volcanogenic sediment-seawater interactions and the geochemistry of pore waters, Chem Geol, 249, pp 321-338, doi:10.1016/j.chemgeo.2008.01.026.

2) Papers that were published as part of my dissertation:

Kutterolf S. Diener R., Schacht U., Krawinkel H. (2008d) Geochemistry and Sandstone Petrography of the Carboniferous Hochwipfel-Formation (Karawanken Mountains, Austria/ Slovenia) – A combined provenance analysis. Sedimentary Geology, 203, 246-266, doi:10.1016/j.sedgeo.2007.12.004

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Abstract

This cumulative work summarizes seven manuscripts published between 2007 and 2012. These studies use marine and on-shore tephrostratigraphy as a tool to quantify and identify the timing, extent, and causes of geological processes taken place at subductions zones.

In many subduction-related regions on Earth, highly explosive plinian volcanic eruptions generate buoyant, tephra bearing eruption columns capable of penetrating up to 40 km into the stratosphere, where they reach a neutral level of buoyancy and spread laterally. Such eruption clouds drift with the prevailing wind over nearby oceans, gradually dropping their ash load over areas that sometimes can be larger than 10^6 km^2. The resulting ash layers are best preserved in non-erosive marine environments and thus provide the most complete record of volcanic activity. Wide aerial distribution across sedimentary facies boundaries, near-instantaneous emplacement, correlative chemical signatures, and the presence of minerals suitable for radiometric dating make ash layers an excellent stratigraphic marker in marine sediments and provide constraints on the temporal evolution of both, the volcanic source region and the ash-containing sediment facies.

On-shore stratigraphic successions of tephra layers are generally based on the distinct composition of tephras. In west-central Nicaragua for example (section 2.1), late Pleistocene to Holocene tephras were emplaced by highly explosive eruptions, with a combined erupted mass of 184 Gt (DRE), that are distributed into 9 dacitic to rhyolitic eruptions (84%) and 4 basaltic to basaltic-andesitic eruptions (16%). Widespread eruptive masses from explosive volcanism are usually underestimated, even when the most distal parts of the on-shore distribution fans, normally not preserved in terrestrial environments, are included. If on-shore tephras can be correlated to offshore deposits like those in Central America (sections 2.2 and 2.3), the revised erupted magma mass show that the tephras account for 65% of the total arc magma output. This enables the minimum estimation of long-term average magma production rate at each volcano and over whole arcs. Using their unique compositional signatures, tephras facilitate the determination of provenance as well as the reconstruction of emplacement processes of volcanoclastic marine sediments, in accordance with regional geotectonic settings (section 2.4). Ash layers in marine sediments offshore Central America can provide time constraints for submarine landslides at the continental slope, as they probably act as weak layers where sliding initiates (section 2.5). Variations in the sedimentation rates on the slope, constrained by bracketing tephras of known age, can be attributed to periods of intense erosion on land likely triggered by tectonic processes. In the case of the incoming plate these changes can be due to changes in bend-faulting activity across the outer rise, which elicit erosion and re-sedimentation. Additionally, ash layers in Central America can help determine the duration of active and inactive periods in the multi-stage growth history of fluid venting sites (section 2.6). Cyclicity in the marine tephra record along the Pacific Ring of Fire yields a statistically significant detection of a spectral peak at the obliquity period, which is related to crustal stress changes associated with ice age mass redistribution and therefore supports the presence of a causal link between variations in ice age climate, continental stress field, and volcanism (section 2.7).

To summarize, the seven manuscripts presented here highlight the benefit of tephrostratigraphy as a major tool in geology, and show that the tephra record on-shore and, especially in the marine environment, have a spectrum of possible applications to decipher the causes and temporal variability of geological processes.

Kurzfassung

Diese kumulative Arbeit umfasst sieben Artikel die zwischen 2007 und 2012 eingereicht oder publiziert wurden. Die behandelten Themen basieren auf die Anwendung von mariner und landgestützter Tephrostratigraphy auf prozessorientierte geologische Fragestellungen an Subduktionszonen mit dem Fokus auf ihre Quantifizierung, Ausdehnung und ihre zeitliche Abfolgen.

Hoch explosive Plinianische Eruptionen, häufig an Subduktionszonen beheimatet, produzieren aufsteigende, tephra-reiche, Eruptionssäulen die in der Lage sind bis zu 40 km in die Stratosphäre einzudringen um sich dort dann lateral auszubreiten. Diese Eruptionswolken werden durch die vorherrschenden Windrichtungen oftmals über die nahen Ozeane transportiert wo sie, nach und nach, ihre Aschefracht über große Areale (>10^6 km^2) „ausregnen" können. Die daraus an der Erdoberfläche resultierenden Aschelagen werden am Besten in nicht-erosiven Bedingungen, wie auf dem Meeresboden, erhalten und stellen deshalb ein nahezu vollständiges Archiv der hoch-explosiven vulkanischen Aktivität einer Region dar. Ihre weiträumige Verbreitung über sedimentäre Faziesgrenzen hinaus, die nahezu unmittelbare Ablagerung nach der Entstehung, die guten korrelativen chemischen Eigenschaften und die vorhandenen radiometrisch datierbaren Phenokristalle machen diese Aschelage zu perfekten stratigraphischen Leithorizonten in marinen Sedimenten. Darüber hinaus liefern sie Informationen über die zeitliche Entwicklung der vulkanischen Quellregionen und der aschehaltigen Sedimentfazies.

Tephraserien an Land werden auf Grund verschiedener Zusammensetzungen unterschieden. In Nicaragua, zum Beispiel (Kapitel 2.1), wurden 184 Gt (DRE) weitverbreitete Eruptionsprodukte von 9 dazitischen (84%) und 4 basaltisch bis basaltisch-andesitischen Großeruptionen abgelagert. Die eruptiven Massen dieses hoch-explosiven Vulkanismus werden häufig unterschätzt, selbst wenn die selten erhaltenen distaleren Landfazies eingeschlossen werden. Können diese landbasierten Tephra-Abfolgen aber mit marinen Tephras korreliert werden, wie dies in Zentralamerika geschehen ist (Kapitel 2.2 und 2.3), zeigen die Ergebnisse, das die Tephren ca. 65% der gesamten magmatischen Produktion ausmachen. Dies ermöglicht auch die Abschätzung von Langzeit-Magmaproduktionsraten für Vulkane und ganze Inselbögen. Durch ihre einzigartige Zusammensetzung kann man, unter Berücksichtigung der regionalen tektonischen Verhältnisse, die Herkunft von Tephren und die Ablagerungsprozesse von marinen vulkanoklastischen Sedimenten bestimmen (Kapitel 2.4). Aschelagen in mittelamerikanischen marinen Sedimenten liefern Zeitmarken für submarine Hangrutsche am Kontinentalhang und dienen eventuell auch als initiale Schwachstelle im Sediment und als Rutschfläche (Kapitel 2.5). Variable Sedimentationsraten am Kontinentalhang, ermittelt mit Hilfe von eingeschalteten Aschelagen bekannten Alters, können außerdem Perioden stärkerer, durch Tektonik ausgelöster, Erosion an Land zugeordnet werden. Variabilität auf der Ozeanplatte hingegen könnte auf wechselhafte Aktivität von „bent faults" am „outer rise" zurückgeführt werden, welche kleinere Erosions- und Resedimentationsereignisse hervorrufen. Zusätzlich kann man mit Aschelagen die Dauer aktiver und inaktiver Perioden von kalten Quellen am Meeresboden bestimmen (Kapitel 2.6). Zyklisches Auftreten von marinen Tephren entlang des Pazifischen Feuerringes korreliert außerdem statistisch signifikant mit Änderungen der Orbitalparameter. Der kausale Zusammenhang zwischen Eiszeiten, Klima, Stressfeld und Vulkanismus besteht in einer erhöhten Eruptionstätigkeit in Folge von raschen Änderungen in der Eis-Ozeanmassen-verteilung und dem assoziierten kontinentalen Stressfeld bei Warmzeiten (Kapitel 2.7).

Die sieben hier präsentierten Manuskripte unterstreichen den Nutzen der Tephrostratigraphie als multiples Werkzeug für geologische Untersuchungen und zeigen ihr Potential um, an Land und im marinen Bereich, Ursachen und temporäre Variabilität in geologischen Prozessen zu entschlüsseln.

1. Insights into tephrostratigraphy

1.1 Introduction

In many active volcanic regions on Earth, highly explosive plinian volcanic eruptions generate buoyant columns that can rise up to 40 km into the stratosphere, where they reach the level of neutral buoyancy and spread laterally. These resulting eruption clouds drift with the prevailing tropospheric and stratospheric winds and will gradually loose their ash load over widespread areas. Tephra layers generated by these dispersal fans are best preserved in marine and lacustrine environments, where erosional effects are limited, and therefore can provide a very complete record of volcanic activity from a specific region. Environments next to volcanic active margins, whether terrestrial, lacustrine or marine, also provide the possibility to host deposits from volcanogenic mass flows, which are initiated or triggered, syn- or post eruptive, at volcanic or continental slopes.

Tephra is a term used to describe the solid material produced from a volcano during an eruption (Thorarinsson, 1944). The term "pyroclast" describes volcanogenic originated material "pyro" (Greek: fire, magma) that is fragmented (Greek: clast, "broken into pieces") during explosive eruptions and transported from a vent to its disposal area (Schmincke, 2004). Tephras (Greek: ash) are defined as unconsolidated pyroclastic particles (e.g. Fisher and Schmincke, 1984; Lowe et al., 2011; Self and Sparks, 1981), and comprise a range of grain sizes ranging from fine dust (ash: <2mm) to large blocks (angular) or bombs (rounded: >64mm) (Froese et al., 2008).

Table 1: Summary for tephrostratigraphic terms and definitions modified after Lowe et al. (2011):

Term	Definition
Tephra	All the explosively-erupted, unconsolidated pyroclastic products of a volcanic eruption
Cryptotephra	Tephra-derived glass shards and/or crystal concentration, deposited in sediment and ice or soil and not visible as a layer or pods to the macroscopic observer (Greek: kryptein, 'to hide').
Tephrostratigraphy	Study of tephra layer sequences and associated deposits (defining, describing, characterizing), their distribution and stratigraphic relationships, as well as their age relations in the field and in the laboratory.
Tephrochronology	Use of tephra layers as isochrons (time-parallel marker beds) to connect and synchronize sequences and to transfer ages to them using stratigraphy and other tools. An age-equivalent dating method.
Tephrochronometry	Obtaining a numerical age or date for a tephra layer.
Pyroclast	Fragmented material from (explosive) eruptions
Ash	Eruptive products smaller than 2 mm; fallout
Pumice/Scoria Lapilli	Foamed magma pieces >2 mm < 64 mm ø, erupted during explosive eruptions; fallout
Block/Bomb	Angular/rounded dense or foamed magma pieces > 64 mm ø, erupted during explosive eruptions or pulses; ballistic transport

Tephrostratigraphy describes the arrangement of tephra layers resulting from pulses of volcanic activity and record a temporal succession within the background sediments (e.g. Fisher and Schmincke, 1984). The two major processes for emplacement of volcanic material are fall and flow deposits. In terms of their regional and supraregional distribution, fall deposits are most interesting because of their instant emplacement, wide aerial distribution, across sedimentary facies boundaries, unique chemical signatures that facilitate stratigraphic correlations, and the occurrence of dateable minerals that make tephras excellent stratigraphic marker beds (Fisher and Schmincke, 1984).
Since the 1980´s there has also been a focus on the identification and classification of cryptotephras, the smallest and most distal tephra deposits that, because of their size and volume, can not always be macroscopically recognized. Cryptotephra derives from the Greek “crypto”, which means hidden, and refers to very fine to fine ash particles (glass shards and minerals that are <125µm) concentrated in different kinds of background material (lacustrine, marine sediments, soils or ice; Alloway et al., 2007; Lowe, 2011; Lowe and Hunt, 2001; White and Houghton, 2006).

On-shore tephrostratigraphy

In the field, tephra beds ranging in thickness from metres to centimetres are mapped, logged and effectively traced from proximal to distal outcrops using their lithological characteristics like color, bedding, sorting and component proportions (pumice types, phenocrysts, vesicularity, vesicle textures) as well as stratigraphic relationships. Tephra-fall beds typically drape over the pre-existing topography and show a decrease in grain size and in heavy component abundance from proximal to distal locations. Tephra layers, usually but not always, become exponentially thinner away from their source (Houghton et al., 2000). While they also lose some of their diagnostic features during this process, tracking their occurrence subaerially is confined to thicknesses in the scale of centimeters. On-shore, tephrochronologists core in lake sediments and peat bogs to retrieve the best possible and most continuous tephra record, even at distal locations (e.g. Bogaard and Schmincke, 2002; Wulf et al., 2008). This high-resolution record of visible tephra layers can range from centimeters to only millimeters in thickness. Such sites complement the normal “terrestrial” field records and enable tephra distribution patterns, so called isopachs (lines of equal tephra thicknesses), to be mapped over much greater distances. This affects also the determination of eruption parameters, as will be shown later.

Off-shore tephrostratigraphy

Tephras preserved in marine sediments provide an excellent archive of explosive eruptions and, due to the advanced drilling techniques in the deep sea drilling programs, also provide potential long-term records of the volcanic activity in specific regions. Detailed description of the tephra layers in this environment is very important, and the distinction between “primary” tephra layers, deposited in a single continuous event from ash fallout onto the sea surface, and “secondary”’ deposits from syndepositional turbidity currents (Fujioka, 1986) developed by slumping of previously deposited ash, must carefully be considered when interpreting the tephra record (Hunt and Najman, 2003; Manville and Wilson, 2004). The occurrence of large submarine slides off-shore Central America (Harders et al., 2010; Harders et al., 2011; Kutterolf et al., 2008c) show scarps on the continental slope that are several meters deep, and therefore facilitate mixing of ashes from several primary tephra layers in the slumped sediments. Additionally, turbidity currents from such events can cross the trench, reach the incoming plate, and cause erosional effects even during the expected homogenous pelagic sedimentation on the oceanic crust. Finally, bioturbation in tephra layers thinner than a few centimeter may obscure individual events (Cambray et al., 1993) since layers become disrupted into lenses or zones of dispersed glass (Manville and Wilson, 2004; Wetzel, 2009). Most of these processes, however, take place soon after emplacement and they probably do not disturb the geochemical integrity of the reworked tephra (Hunt and Najman, 2003).

The use of distal marine tephras for volume determinations through isopach maps is sometimes problematic in that it underestimates tephra layer thickness due to compaction and dissemination of tephras in the sediment. To avoid some of these uncertainties the use of isomass maps have been developed, and thicknesses are then replaced by mass per unit area (e.g. Bonadona, 2006). However, the detailed description and logging of deposit density, particle density, and tephra (or cryptotephra) accumulation per unit area is a prerequisite to use isomass distributions (Bonadona, 2006).

1.2 Tephrochronology

Tephrochronology describes the use of tephra layers as isochrons to connect sequences in different places by providing precise chronostratigraphic tie-points (Alloway et al., 2007). After Lowe (2011), tephrochronology is a inimitable stratigraphic approach for correlating, dating, and synchronizing geological, palaeoenvironmental, or archaeological sequences or events by using the known relative stratigraphic order and physical properties evident in the field, together with compositional geochemical fingerprinting obtained from laboratory analyses of correlative tephras.

The accuracy of tephrochronology can be improved, and the method provides its best results, when it is done by direct, multiple, dating of tephra layers by one or more dating methods (Lowe, 2011). Unless evidence for reworking is found a tephra layer is assumed to have the same age wherever it occurs and thus, once characterized or 'fingerprinted' by its mineralogical and geochemical properties, provides a time-parallel stratigraphic marker bed or isochron (Froese et al., 2008). The age of a "marker bed" can be transferred regionally or even across inter-continental scales from one location to the next by chemical fingerprinting, and results in a network of marker beds and a regional tephrostratigraphy. Age transfer is a key issue in tephrochronology, but can be effectively applied because tephras are transported to–and deposited at–their final location nearly instantaneously (in geological time-scales) after they have been generated by volcanoes (e.g. Carey, 1997; Cole-Dai et al., 2009; Harris et al., 1981; Manville and Wilson, 2004; Miller and Casadevall, 2000; Mills, 2000; Robock, 2000; Rose and Durant, 2009; Wiesner et al., 2004; Zielinski et al., 1997a; Zielinski et al., 1997b).

Tephra studies therefore play an important role in establishing a chronostratigraphic framework for volcanology over extensive areas. Using tephra layers as a chronological tool was first developed in Iceland (Thorarinsson, 1944, 1951), and has been applied to other volcanic settings all over the world (Alaska, New Zealand, Mexico, Mediterranean) and, as it will be shown here, it can also be applied in Central America. While tephrochronology was first used in areas proximal to volcanic centers, medial, distal and very distal locations (>2000 km) are now becoming a focus of stratigraphic correlators (e.g. Alloway et al., 2007; Hunt, 1999). Distal tephra deposits can extend over thousands–or even hundreds of thousands–square kilometers, and uniquely provide one of the most robust stratigraphic and dating tools available to geoscience (Froese et al., 2008).

Macroscopic recognition of distal tephra deposits in marine or lacustrine sediments, soils and ice cores becomes more difficult, as the smallest particles are collected in more and more thinner deposits (Lowe and Hunt, 2001). These "hidden" distal tephras (Dugmore, 1989) have now been named cryptotephras, and have been a new focus for tephrochronologists studying in northern Europe, Scandinavia, New Zealand and elsewhere (e.g., Davies et al., 2002; Davies et al., 2007; Davies et al., 2004; Turney et al., 2004; Wohlfarth et al., 2006)

Although well characterized tephras enable sequences to be aligned with remarkable precision and reliability, misidentification, reworking or miscorrelation can produce significant problems in synchronization and age modeling, as discussed extensively in Lowe (2011) and in Kutterolf et al. (2008a). Using detailed sedimentological analyses of the tephras and surrounding sediments, as well as modern analytical methods, and multiple, independent, correlation methods and tools will help to avoid such misidentification and miscorrelations.

1.3 Tools in tephrostratigraphy

Modern analyses, together with detailed field work and drilling techniques that provide the best and most complete sediment recovery, include mineralogical examination (petrography) or geochemical analysis of glass shards or crystals using an electron microprobe, laserablation-based mass spectrometry or the ion microprobe.

Field work

Tephrostratigraphic field work is nearly the same as the typically geological field work, and relies in the observation, description and detailed logging of the depositional tephra successions in outcrop to construct maps with lines of equal thicknesses and grain sizes (isopach and isopleth maps) of tephra layers. Field correlations are then based on modal compositions, textures of pumices, sedimentary structures, relative positions, occurrence of unconformities and on the nature of intercalated sediments.

Coring

The drilling in marine environments by the Deep Sea Drilling Project (DSDP), Ocean Drilling Project (ODP), and the Integrated Ocean Drilling Project (IODP) facilitates coring into the ocean floor with deep penetrations up to several hundred meters. Coring is therefore very well suited to extend tephrostratigraphy to great ages (in the million-year age range). Unfortunately, due to financial reasons, its application is limited to only a few sites. Although piston and gravity cores reach only up to 50 m deep in soft sediments, limiting tephrostratigraphy to ages less than 10^6 years, multiple core locations can be used to obtain lateral profiles or arrays of sections. This technique provides additional insights into lateral stratigraphic changes or local erosional events. However, to assure best recovery results in both gravity coring and deep sea drilling, core locations must be chosen on the basis of high-resolution bathymetric maps and/or seismic profiles to avoid, for example, erosional features produced by turbidity currents on the continental slope and on ridges outside submarine canyons.

Marine core sampling and logging

Visual identification and sampling of tephra layers can easily be performed when the ash forms mm- to cm-thick distinct and undistorted layers. Tubes and scoops, or micro drill-cores for hardened material are the preferred sampling methods in the working half of the core, complemented by detailed

description of the sediment structures and textures in the archive half.
In slope settings and rough ocean plate morphology, mass wasting processes redistribute the ash and may make visual recognition in core sections difficult. Core logging is an additional tool for the visual core description and is becoming more and more popular in tephrostratigraphic research of marine and lacustrine environments, as they can help in the identification of both, distinct layers and dispersed ashes, in sediments. Core logging techniques facilitate, and sometimes is the only way for, the detection and mapping of cryptotephras (e.g. Peters et al., 2010). Common analytical facilities include field or ship-board instruments such as core scanners and magnetic susceptibility meters. Standard core logging parameters include P-wave velocity, sediment density from gamma-wave attenuation, magnetic susceptibility, XRF-based core scanning, and scanning X-ray tomography. Whereas these last two are efficiently used on large drill ships like the RV CHIKYU, the most sensitive method to identify volcanic ashes in standard shipboard laboratories is magnetic susceptibility. This method describes the degree to which a material can be influenced by a magnetic field, and is expressed as the intensity ratio of the sediment magnetization to an external magnetic field. The magnetic susceptibility value of natural samples is proportional to the volume fraction of magnetic minerals (Blum, 1997) and is therefore also a measure of the amount of ash in the sediments. Compared to background sedimentation, denser mafic tephras are easily recognized by magnetic susceptibility because of their higher amount of magnetic minerals (e.g. magnetite, chromite, hematite, titano-magnetite). In contrast, felsic tephras that are rich in feldspar, glass, and related weathering products show low or even "negative" magnetic susceptibility values (Hunt et al., 1995). As a consequence, core-log signatures of felsic ash show low or lower background magnetic susceptibility values associated with distinct peaks in density whereas mafic tephras peak in both values.

Analytical correlation techniques (fingerprinting)

Several analytical methods are used to characterize Tephra. This 'fingerprinting' approaches are applied on individual glass shards and on magmatic minerals (Table 2), and are always performed in conjunction with stratigraphic, palaeoenvironmental (sometimes archaeological), and chronological criteria (Lowe, 2011). Although there are a lot of different available methods, petrographic and geochemical analyses are the most powerful and the preferred tools to establish correlations between marine/lacustrine and terrestrial tephras. Petrography identifies typical mineral assemblages and textural characteristics of ash particles, and micro-analytical techniques, are applied to all samples, sometimes only after enrichment during sample preparation (e.g. in dispersed sediments, cryptotephras). Since chemical separation methods has shown some effects on glass stability during electron microprobe analysis (e.g. Blockley et al., 2005; Dugmore et al., 1992), its application during the cleaning and enrichment process of glass shards should be avoided as much as possible.
The most widely used micro-analytical technique at the moment is the electron microprobe (EMP), which determines the concentration of major, minor, and some trace elements in volcanic minerals and glasses that are embedded with epoxy resin (Araldite) in acrylic glass tablets containing pre-drilled holes. The setup conditions vary between laboratories but typically 10 to 13 major and minor elements (e.g. Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K, and P, complemented by S, F, and Cl) are analyzed. This analysis uses intensities from X-rays and their element-specific energies and wavelengths that are produced by a focused electron beam on the sample surface. Measuring, calibration and standardiza-

tion conditions used during the investigations in this thesis are described in detail in Kutterolf et al. (2011) and follow the procedures established within the GEOMAR EMP laboratory, which is equipped with a JEOL JXA 8200 wavelength dispersive electron microprobe. To avoid the effects of variable primary (magmatic) and secondary (alteration) hydration, and to enable valid comparisons of measurements, all analyses are normalized to 100% volatile-free basis.
The advantages of applying single point analyses versus bulk rock analyses on the investigated tephras are the detection of components in compositionally zoned magmas, and the identification of material from different eruptions in ash beds that were mixed by reworking.

Table 2: Summary of commonly used analytical fingerprinting methods in tephrostratigraphy and their respective components (after Lowe, 2011).

Tephra components and properties	Measured components	Methods of analysis
Glass shards	Major- and trace elements	EMP, LA-ICPMS, SIMS
Shard morphology	Glass shard shape, vesicle structures	Optical microscope, SEM
Fe-Ti oxides	Major- and minor elements, crystallization temperatures, oxygen fugacities	EMP, Mössbauer spectroscopy
Ferrormagnesian minerals *(px, am, ol, bi)*	Major-, minor and trace elements, crystallization temperatures, pressures, water content	Petrographic microscope, EMP, LA-ICPMS, SIMS
Feldspars	Major-, minor and trace elements, crystallization temperatures, pressures, water content	EMP

When variations in the analyzed major elements of glasses and/or minerals are not sufficiently diagnostic, trace element compositions of juvenile matter can be determined. In older tephras particularly, immobile trace elements are important since they are resistant during alteration and thus are especially well suited for geochemical correlation (Clift and Blusztajn, 1999; Pearce et al., 1999; Schmincke, 2004). Initial bulk analyses of trace elements and REE's using glass-shard accumulations have now been replaced by new developments like Laser Ablation Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS) or by Secondary-Ion Mass Spectrometry (SIMS, ion probe). These techniques have completely revised and upgraded trace element analysis of tephras by providing an efficient and precise method for determining abundances of a wide variety of trace elements. This facilitates the correlation and discrimination of individual tephras having similar mineralogy or provenance (Bryant et al., 1999; Pearce et al., 2007; Westgate et al., 1994). During LA-ICPMS measurements the knowledge of at least one element (e.g. Si, Ca) in the sample, acting as an internal standard, is required to calibrate the analyses to homogeneous trace element standard reference materials, such as National Institute of Standards and Technology 'Trace Elements in Glass' standard NIST 610 or NIST 612 (Pearce et al., 2007). In the past around 30 trace elements have been determined from single glass shards, with sizes down to ~40 µm in diameter, in about 3 min (Pearce et al., 2007). Recently, according to Pearce et al. (2011), analyses of glass shards with ablation craters as small as 10 µm in diameter can still provide high quality data. Until now, smaller beam sizes reached the limitations of spatial resolution in the technique due to the physical process of ablation and the accompanying elemental fractionation. Therefore although less allocable, more expensive, and slower than LA-ICPMS systems, the ion probe has the advantage of less destructive sputtering to remove sample material from glass shards into the mass spectrometer, which is important when analyzing cryptotephra.

Statistical techniques to aid correlation

To use all measured data at once, according also to their weighted correlative importance, application of statistical techniques are coming into focus for correlation methods in tephrostratigraphy, since the classical graphical correlation methods are limited by a certain amount of simultaneously used elements. Therefore numerical correlation techniques use similarity coefficients (SC) and coefficients of variation (CV) to compare the whole geochemical data set. The results can be clustered into dendrograms according to geochemical similarity and assist correlations in tephrostratigraphy (e.g., Brendryen et al., 2010; Kuehn and Foit Jr, 2006). Jordan et al. (2006) and Kutterolf et al. (2008a) use cluster analysis, where a distance matrix from overall differences in the compositions of samples has been established to help correlate tephras. The canonical Discriminant Function Analysis (DFA) is another statistical technique related to principal component analysis that reduces the dimensionality of data (such as compositional analyses) with a large number of independent variables (Lowe, 2011), resulting in one or two canonical variables containing the whole compositional information (e.g. Molinaroli et al., 1991).

Direct and indirect dating of tephras

Numerical ages on tephras/cryptotephras are essential to establish a detailed tephrochronology and therefore also a large-regional tephrostratigraphy. Using a range of techniques including radiometric (e.g., radiocarbon, single mineral dating, fission track, luminescence), incremental (e.g., ice cores, varves, dendrochronology), age-equivalence (e.g., orbital tuning, magnetopolarity, palynostratigraphy, sedimentation rates), and historical observation, tephras can be dated directly or indirectly (Drexler et al., 1980; Kutterolf et al., 2008a; Ledbetter, 1982; Lowe, 2011; Schmincke, 2004; Wulf et al., 2004). The most commonly used method to date tephras include direct radiometric dating (^{14}C, U/Th, K/Ar and single-crystal laser fusion 40Ar/39Ar analysis, zircon- and glass-based fission-track analysis) using primary minerals and material (such as zircon, hornblende, K-feldspar, biotite, quartz, foraminifers) from within the tephra layer or the underlying sediment. Nevertheless, for tephras originated in the last ca. 55,000 years, the ^{14}C dating still remains the most important technique to establish eruption ages (Alloway et al., 2007). Sedimentation rates, oxygen isotope stratigraphy, varve chronology and magnetopolarity can be used to make first order estimations of tephra ages by applying constant age models in the background sediments and therefore the position of the tephra within. Nevertheless, as will be shown below, sedimentation rates can be very heterogeneous in shorter time scales ($<10^4$ years) and this method becomes more precise when approximating ages in long living ($>10^5$ years) depositional systems, since than smaller variations are balanced over time. Ideally, a combination of direct (tephras) and indirect (sedimentation rates) dating techniques can achieve a reliable and feasible, but still affordable, high resolution age model to constrain unknown tephra ages, even in variable depositional settings.

1.4 The Pacific Ring of Fire

All manuscripts introduced in this habilitation thesis are geographically constrained to the so-called "Pacific Ring of Fire" (ROF; Figure 1). The ROF results from plate tectonics and, specifically, from the movement and collisions of lithospheric plates. The ROF extends from New Zealand, along the eastern edge of Asia, including the Philippines and Indonesia, north across the Japanese islands and Aleutian Islands of Alaska, and south along the coast of North, Middle and South America (Figure 1). Subduction zones characterize the geotectonic setting around the ROF; the eastern most arc systems are generated by the subduction of the Nazca Plate beneath the westward moving South American Plate, and the Cocos Plate beneath the Caribbean Plate in Central America, respectively. To the north-east a portion of the Pacific Plate, together with the small Juan de Fuca Plate is being subducted beneath the continental North American Plate. The Aleutian Island arc in the northern ROF, the Kamtchatka Peninsula, and the Northern Japanese islands to the northwest, are the continuation of the subduction between the Pacific Plate beneath the North American Plate.

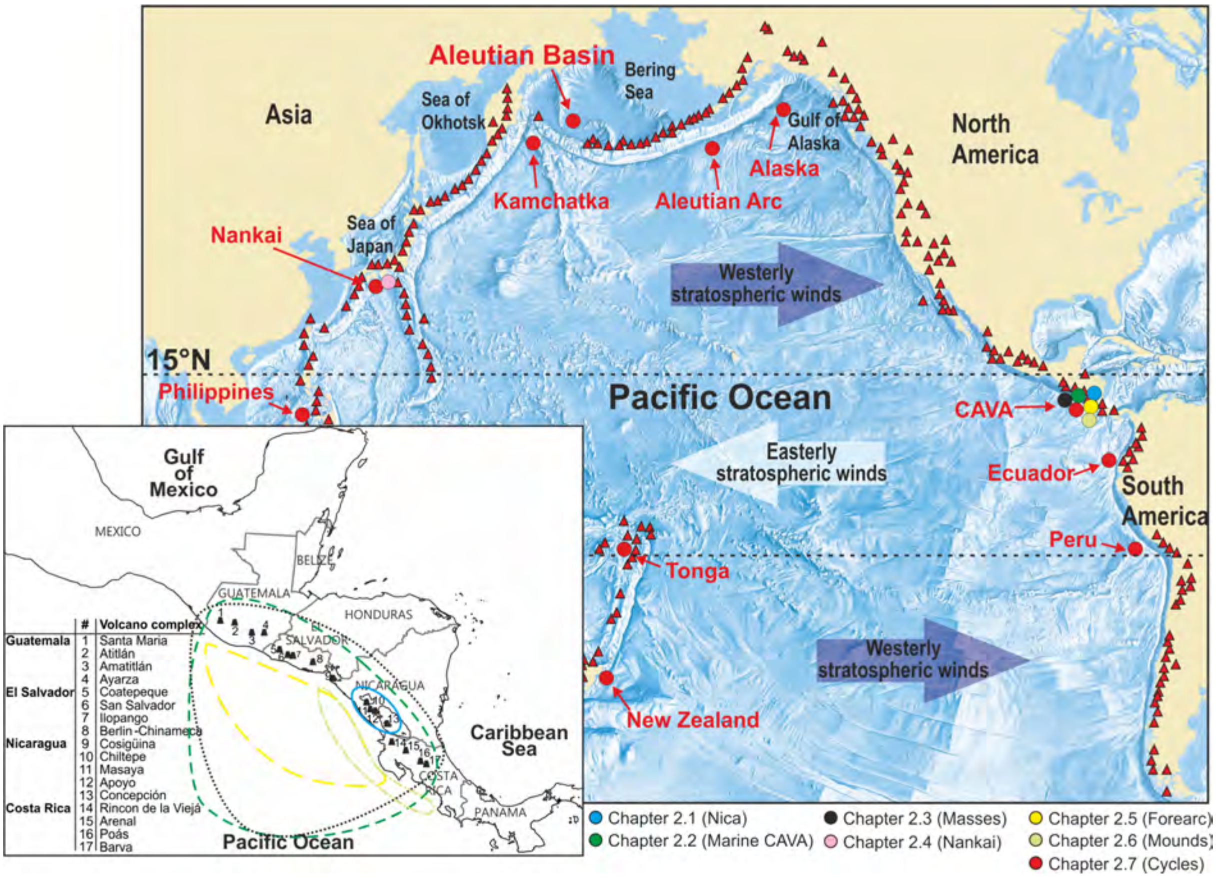


Figure 1: Bathymetric map of the Pacific Ocean with red triangles indicating active arc volcanoes along the Pacific Ring of Fire. Different colored dots mark the regions, which are covered within the publications introduced in this thesis. Arrows and dashed lines mark predominantly global stratospheric wind directions. The blow up in the lower left corner shows a map of the Central American region that focuses in more detail on the studied areas of this region within this thesis.

Further southwest the ROF is more complex with the Philippian Plate and Australian Plate colliding with the Pacific plate and resulting in the Mariana Islands, the Philippines, Tonga, and New Zealand. Because of active plate tectonics, the ROF is an area where a large number of earthquakes and volcanic eruptions occur. It accounts for about half of the global length of 44,000 km of active subduction and about 81% of the world's largest earthquakes, and approximately 75% of the world's active and dormant volcanoes occur along the Ring of Fire (USGS). This long living system has produced large subduction related volcanic eruptions for at least 20 Million years. Using the extensive archive of sediments from deep sea drilling projects (DSDP, ODP, IODP) early studies have already revealed the episodic nature of this circum-Pacific volcanism. Volcanism on long time scales was identified by periods of increased ash-layer frequency in the Quaternary, latest Miocene to early Pliocene (3-6 Ma), late Miocene (~8-11 Ma) and middle Miocene (~14-16 Ma) (Cadet and Fujioka, 1980; Cadet et al., 1982a; Cambray and Cadet, 1994; Hein et al., 1978; Kennett et al., 1977; Kutterolf et al., 2007b; Ledbetter, 1982; Pouclet et al., 1985; Prueher and Rea, 2001; Sigurdsson et al., 2000).

2. Applications of tephrostratigraphy

2.1 Late Pleistocene to Holocene temporal succession and magnitudes of highly-explosive volcanic eruptions in west-central Nicaragua.

Standard on-land tephrostratigraphy outcrop conditions often benefit from modern road construction by providing a continuous amount of fresh scarps in roadcuts. In the tropical regions of the ROF, with their extensive ground vegetation, roadcut geology is necessary to record complete tephra sequences within the Holocene. In Nicaragua, particularly, this factor has facilitated the detailed revision of older stratigraphic work by Bice (1985), Williams, (1983), and Sussmann (1985), and the results summarize the benefits of extensive on-land tephrostratigraphy for volcanological and hazard-related research over an entire volcanic arc segment.

The active volcanic chain in Nicaragua is part of the Central American Volcanic Arc (CAVA), which has one of the highest densities of active volcanoes in the world (Völker et al., 2011). The Central American Volcanic Arc (CAVA) extends from Costa Rica to Guatemala and lies 150-200 km away from the Middle America trench where the Cocos plate subducts beneath the Caribbean plate at a convergence rate of 70–90 mm/year (Barckhausen et al., 2001; DeMets, 2001). The arc is tectonically segmented (Stoiber and Carr, 1973) due to slightly oblique subduction (DeMets, 2001).

Explosive eruptive activity in Nicaragua in the late Pleistocene to Holocene included a range of strombolian to violently surtseyan to sub-plinian and plinian eruptions. These large-magnitude and widespread fallout-bearing eruptions of west-central Nicaragua, which originated from both, felsic and mafic volcanoes, emplaced also voluminous ignimbrites generated by pyroclastic flows. Assessing hazard scenarios from explosive volcanic activity in densely populated areas requires knowledge about how the temporal evolution, style, intensity, and magnitude of eruptions vary at each contributing volcanoes. Kutterolf et al. (2007a) therefore focuses on field aspects of the Nicaraguan tephra succession, particularly on stratigraphic relationships and tephra dispersal characteristics. Together, these allow the determination of the dynamic parameters of eruptions and their related emplacement processes. Altogether these data contribute to future hazard assessment studies of large eruptions in this region (e.g. Freundt et al., 2006a). Furthermore, petrogenetic relationships within and between Nicaraguan volcanic systems are based on this fundamental study (Freundt et al., 2010; Geilert et al., 2012; Kutterolf et al., 2011; Pérez and Freundt, 2006; Peréz et al., 2009; Schmincke et al., 2009; Schmincke et al., 2010), and estimations of individual and long-term cumulative fluxes of volatiles into the stratosphere by these eruptions are used to evaluate the climate impact of paleo-eruptions from the CAVA (Kutterolf et al., sub; Metzner et al., 2012).

The stratigraphic succession of widespread tephra layers in west-central Nicaragua were emplaced, mainly, by three volcanic centers that have been active through the Late Pleistocene to Holocene: the Chiltepe volcanic complex, the Masaya-Las Sierras Caldera system and the Apoyo Caldera. Additionally to the tephras known from the literature (Bice, 1985; Sussman, 1985; Williams, 1983), Kutterolf et al. (2007a) newly identified and radiocarbon dated a number of widespread tephras in western Nicaragua, and integrated them into a new stratigraphic framework (Figure 2). Stratigraphic correlations between outcrops are based on distinct compositions and structures of tephra layers, encompassing field characteristics like internal sedimentological changes in the individual tephra successions, mineralogy, and clast textures. This field-based parameters are then assisted by lab-based compositional changes in bulk-rock, glass and mineral chemistry.

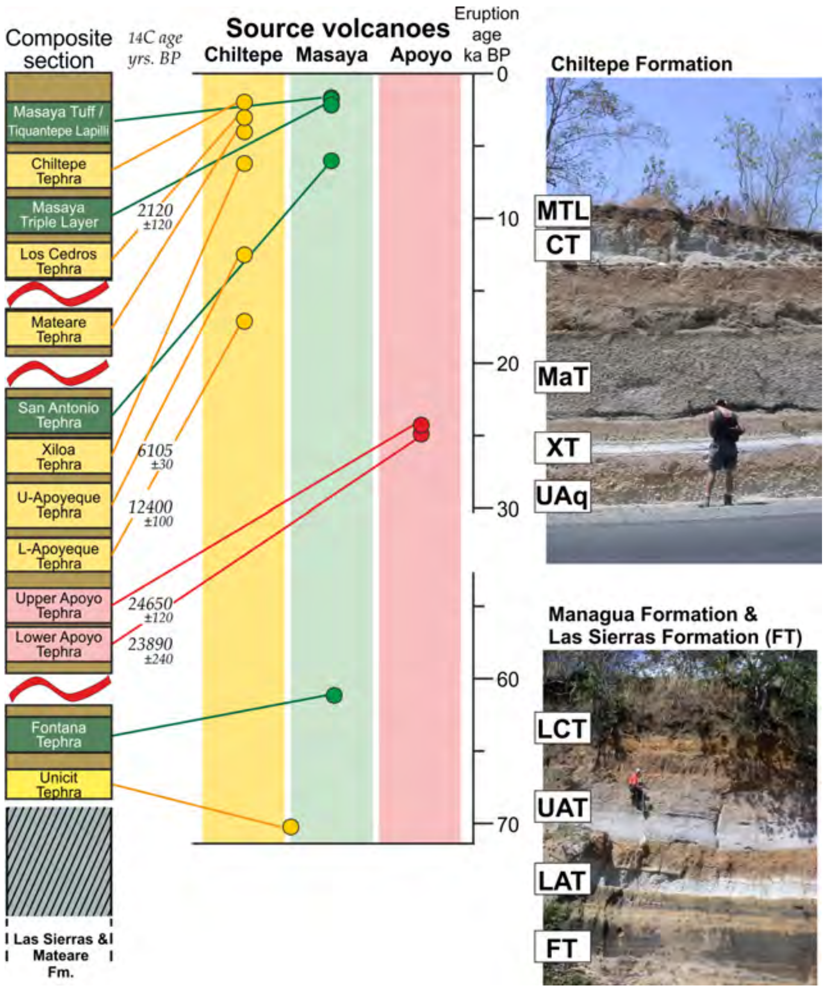


Figure 2: Composite stratigraphic successions of Late Pleistocene/Holocene tephras from highly explosive eruptions in west-central Nicaragua and underlying older Las Sierras und Mateare Formation. Colored points in the boxes indicate the respective sources of the tephras and their temporal occurrence within the regional stratigraphy. Major erosional unconformities are indicated as red wavy lines. Photographs to the right are showing a composite tephra sequence of the Chiltepe (top; Loc. A96 between Mateare and Nagarote at E0558032, N135552) and Managua and Las Sierras Formation (bottom; Loc. A55 in San Marcos at E0586466, N1318229). LCT= La Concepción Tephra, UAT= Upper Appoyo Tephra, LAT= Lower Apoyo Tephra, FT= Fontana Tephra, CT=Chiltepe Tephra, MaT= Mateare Tephra, XT= Xiloá Tephra, UAq= Upper Apoyeque Tephra.

The dispersal area, as well as thickness and grain size changes (isopach and isopleth maps) of all individual tephras, were mapped and used to calculate erupted volumes and eruption parameters (Figure 3) based on methods from the literature (Carey and Sparks, 1986; Fierstein and Nathenson, 1992; Pyle, 1989; Wilson and Walker, 1987; Woods, 1988). The nine dacitic to rhyolitic and the four basaltic to andesitic highly explosive eruptions from the three volcanic complexes have produced a total volume of at least 37 km^3 of widespread tephra on-land in west-central Nicaragua (Kutterolf et al., 2007a), as well as at least 48 km^3 distally in the Pacific Ocean, which will be discussed in the next two setions (Kutterolf et al., 2008a; Kutterolf et al., 2008b). Bulk-rock densities together with data from the most Northern Cosiqüina and most Southern Concepción volcanoes (Metzner et al., 2012), yield 156 Gt of erupted magma mass (Dense Rock equivalent) for a total of 19 eruptions in the last 70 ka at the Nicarguan arc. Eruption columns of the plinian to phreatoplinian eruptions reached variably high altitudes (14 to 40 km) into the stratosphere (Figure 3). Therefore, next to the deposition of a high portion of their solid material into the Pacific Ocean, all these eruptions carried much of their exsolved volatiles into the stratosphere (e.g. Metzner et al., 2012). Comparing the downwind shape of the individual fall-out fans of the tephras with present-day, seasonally changing height-dependent wind directions (NOAA-CIRES, 2001), facilitated a first order estimation of whether the eruptions took place in either the rainy or the dry season. The tephra succession shows that 8 out of the 13 eruptions occurred during the rainy season. Furthermore, the complete tephrostratigraphy also documents and dates two major tectonically and/or climate induced phases of erosion in western Nicaragua at >17 ka and between 2 and 6 ka ago.

The sequence of eruptions at volcanic centers also facilitate the evaluation of regular patterns in eruptive behavior that can be extrapolated into the future. For the dacitic Chiltepe complex for example, the good record (6 eruptions) of the eruptive behavior over the last 17 ka cautiously suggests this complex is a likely candidate for the next big silicic eruption in Nicaragua. In contrast, the silicic Apoyo caldera produced a large plinian double-eruption 24 ka ago and its very long repose times, on the order of 10^4 years, do not allow a similar appraisal. The Masaya caldera on the other hand had generated 3 highly explosive basaltic eruptions since ~ 6 ka, the possible time of the recent Caldera formation, and experienced only small scaled but frequent effusive and explosive eruptions, mainly inside the Caldera, during the last ~ 1.8 ka. The change in eruptive style makes it difficult to evaluate a regular eruption behavior that can be extrapolated into the future. Nevertheless, the complete understanding of the older Las Sierras Caldera System and its frequent, most probably, highly explosive eruptions could be a fundamental step in the understanding of this mafic Caldera system.

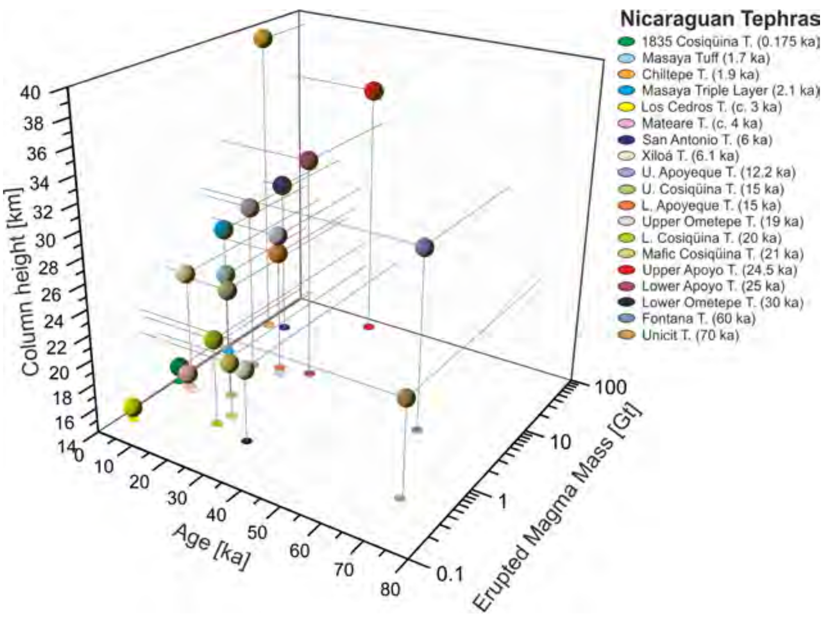


Figure 3: Three-dimensional diagram showing age in ka, erupted magma mass in kg and maximum eruption column height in km for each Nicaraguan Plinian eruption investigated after Kutterolf et al. (2008a, 2007a) and Metzner et al. (2012). All eruption columns penetrate the tropopause with an altitude of 15 km in Nicaragua. Grey bars indicate the intersection of each data point with the individual diagram planes.

With regards to a more regional picture, comparison of the erupted masses from the wide dispersed Nicaraguan tephra sheets to volcano edifice volumes and masses determined by Carr et al. (Carr et al., 2003; Carr, 1984; Carr et al., 1990; Carr et al., 2007), yield up to five times the mass of their parental volcanic edifices. Tephras, therefore, represent a significant, amount of the erupted mass of arc volcanism, and become even more important when the most distal portions of the fans distributed over the ocean area at the ROF are included.

2.2 Pacific off-shore record of plinian arc volcanism in Central America: 1. Along-arc correlations

This manuscript is a follow up of section 2.1 and extends the tephrostratigraphy of plinian and ignimbrite-forming eruptions at CAVA off-shore Nicaragua and includes tephra dispersal along the entire on-shore and off-shore portion of the CAVA going back to at least 450 ka. A number of previous studies can be found in the literature that used ODP/DSDP/IODP and gravity cores to investigate tephra layers off-shore Central America (Bowles et al., 1973; Cadet et al., 1982a; Cadet et al., 1982b; Clift et al., 2005; Drexler et al., 1980; Hahn et al., 1979; Ledbetter, 1982; Pouclet et al., 1985). Although these studies identified the Los Chocoyos ash from Atitlán Caldera in Guatemala as a widespread marker bed, which can be found at very distal sites off-shore Costa Rica to Equador and in the Caribbean basin, none of these studies performed a complete, comprehensive transnational or regional tephrostratigraphy for the CAVA. Other correlations remained uncertain because of the lack of reference data from deposits on-shore and because of provenance limitations due to analyses of only the major elements.

Kutterolf et al. (2008a) incorporated both, an extensive tephra sample suite from on and off-shore locations and from explosive eruptions of the entire CAVA (Chiesa, 1991; Chiesa et al., 1992; Freundt et al., 2006b; Hart, 1983; Kempter et al., 1996; Kutterolf et al., 2007a; Mehringer et al., 2005; Newhall, 1987; Peterson and Rose, 1985; Rose, 1987a, b; Rose et al., 1999; Vogel et al., 2004; Vogel et al., 2006), as well as a complete set of major and trace element glass and mineral data that characterize the field tephras and the correlative marine ashes. Since magmatic

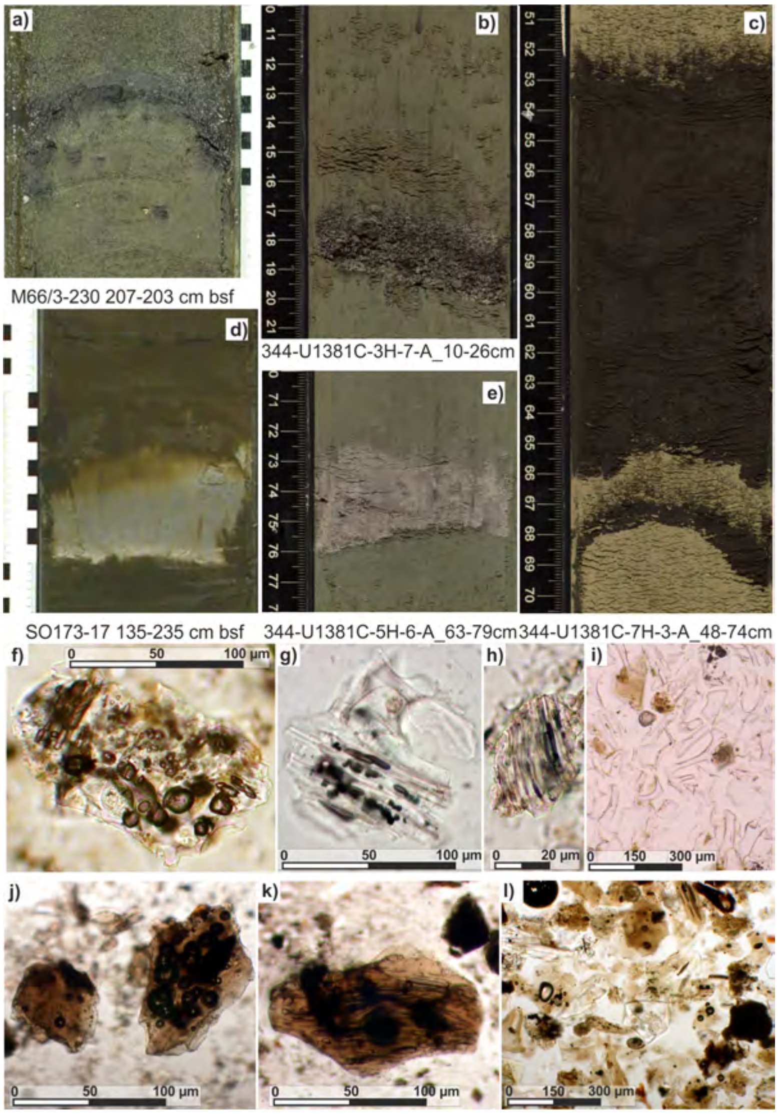


Figure 4: a) through e) Photographs of selected primary mafic (black) and felsic (greyish/pinkis) ash layers. Smear-slide micro-photographs showing glass-shard textures of marine ash layers are given in f) SO173-17/42 cm bsf: vesicular pumice remnant; g) M66-222/237 cm bsf: tubular to cuspate shard; h) SO173-17/41 cm bsf: deformed tubular pumice; i) M66-229/535 cm bsf: large blocky cuspate glass shards; j) M66-223/305 cm bsf: blocky sideromelane shard with and withoutout vesicles; k) M66-222/436-441 cm bsf: elongated vesicles in sideromelane shard; l) 222/517-518 cm bsf: different mafic glass shards in one sample.

compositions at the CAVA change systematically along the arc in response to changing subduction conditions (Carr et al., 2003; Carr, 1984; Carr et al., 1990; Carr et al., 2007; Feigenson et al., 2004; Hoernle et al., 2008; Hoernle et al., 2002; Patino et al., 2000), and there are local variations due to magmatic differentiation, this compositional diversity is extremely useful for stratigraphic correlations.

The marine part of the study from Kutterolf et al. (2008a) is mainly based on 213 identified white to greyish pink up to black 0.5 to 15 cm thick ash beds from 56 sediment gravity cores of 1.5 to 11 m in length that contain characteristic transparent to brownish juvenile glass shards (Figure 4). These cores were taken on the continental slope and on the incoming Cocos Plate during 4 cruises (RV METEOR: M54, M66a,b; RV SONNE: SO173) along the Central American Trench, from Costa Rica to southern Guatemala.

By using the new and extensive reference data base of bulk rock, glass and mineral compositions of stratigraphically controlled widespread, mostly plinian, on-shore CAVA tephras, 129 correlations between individual cores and to 11 Nicaraguan, 8 El Salvadorian, 6 Guatemalan, and 1 Costa Rican plinian eruptions have been established. Compositional correlations were assisted by structural and lithological characteristics as well as by stratigraphic relationships (e.g. proportions of components such as minerals, glass shards, volcanic lithics, other clastic sediment, biogenic material, vesicularity, vesicle texture of pumice fragments, known stratigraphic relationships from land). Such observations helped to support correlations, but glass chemical compositions, assisted by multi-element hierarchical cluster analysis (e.g. Bice, 1985; Jordan et al., 2006), proved to be the most distinctive characteristic.

Eighty-two felsic and mafic, >200 ka old tephras, in cores off-shore Central America could not be correlated to individual tephras from land. Therefore Kutterolf et al. (2008a) used comparisons with the systematic along-arc variation of trace-element characteristics of arc rocks to localize some provenance information for the possible sources (Figure 5). Since the used along-arc variations of Zr/Nb, Ba/La and Ce/Yb in Kutterolf et al. (2008a) are roughly symmetrical, such that these parameters do not efficiently distinguish between Guatemalan and Costa Rican compositions, the authors also considered the distance between the core location and the possible sources. Together with thickness and grain size data they evaluated if the proposed correlations are reliable. With this information, ten additional correlations

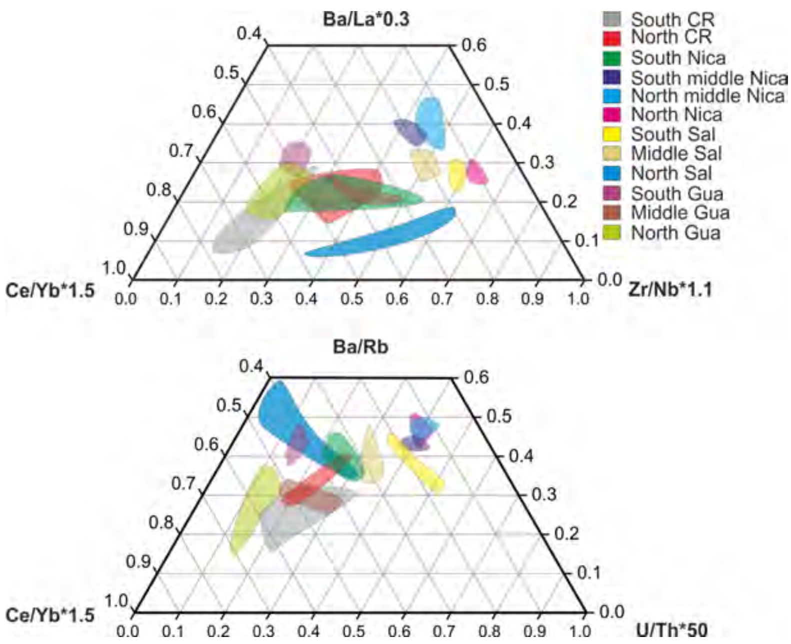


Figure 5: Provenance diagram for unknown sourced tephras to volcanic regions from Central America using the combination of distinctive trace element ratios (e.g. Ba/La, Ce/Yb, Zr/Nb, Ba/Rb, U/Th) of Holocene to Upper Pleistocene evolved tephras along the CAVA.

have been made to older Guatemalan and even Mexican volcanic centers. Approximately 20 and 25 marine ash layers can be attributed to sources from El Salvador and Nicaragua respectively, and seven marine tephras have the trace element signatures of Costa Rica volcanoes. Overall, the presence of these off-shore ash layers shows that there were more highly explosive eruptions in Central America in the past 450 ka than previously thought. Additionally, pelagic sedimentation rates derived from correlations to radiometrically dated tephras on-shore allowed the determination of ten new dates for previously undated tephras (Figure 6). New ages were ~1.8 ka for the Masaya Tuff/Ticuantepe Lapilli, ~1.9 ka for the Chiltepe Tephra, ~17 ka for the Lower Apoyeque Tephra, ~19 ka for the dacitic plinian eruption of Concepciòn volcano, 21-22 ka for mafic Cosigüina tephras, ~39 ka for Mixta Tephra, ~43 ka for TB4-Tephra, ~51 ka for Conacaste and E-Tephra and ~60 ka for the mafic plinian Fontana Tephra. The combined marine and terrestrial records of Kutterolf et al. (2008a) in Central America yielded, for the first time, a tephrostratigraphic framework for the Central American volcanic arc from Costa Rica to Guatemala.

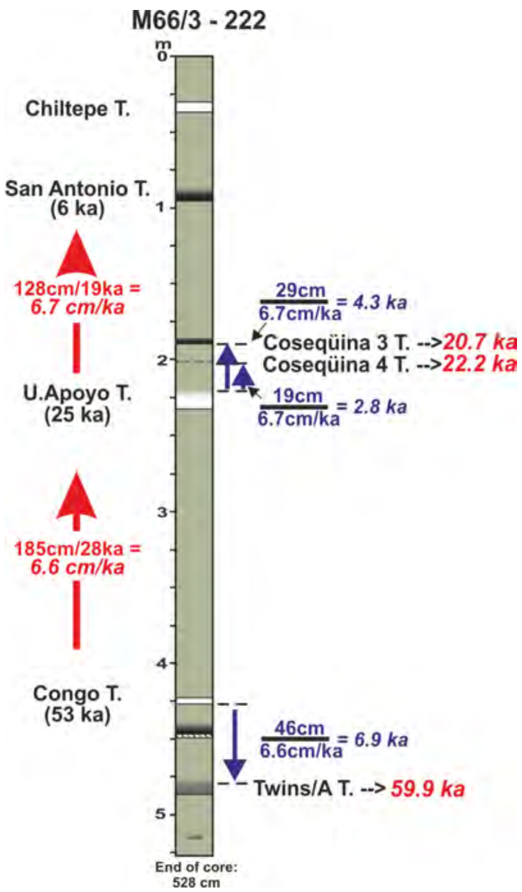


Figure 6: Exemplarily shown stratigraphic sequence of pelagic sedimentation from the incoming plate offshore Nicaraguan/El Salvadoran border (M66-core 222) showing a homogenous sedimentation rate (red arrows and belonging calculations) using the correlation to well-dated tephras on land (6 ka old San Antonio Tephra, Nicaragua; 24.5 ka old Upper Apoyo Tephra, Nicaragua; 53 ka old Congo Tephra, El Salvador) as time markers. Vice versa this sedimentation rate can be used to estimate ages (blue arrows and belonging calculations) for eruptions that not have been feasible to date onland (Cosequina 3 and 4 Tephra, Nicaragua; Twins Tephra, El Salvador).

2.3 Pacific off-shore record of plinian arc volcanism in Central America: 2. Tephra volumes and erupted masses

Subduction zones are often studied to quantify the underlying processes of these regions where material is consumed (input) but also generated (output). The most obvious output is the flux of magma through the volcanic arc, which can also be used to determine the associated output fluxes of volatile material. Next to previously investigated volcano edifice volumes, the widespread tephras appear to account for a large part of the total magma output (Kutterolf et al., 2007a, section 2.1). In order to further assess variability between entire arc segments, or even in an entire arc system, the erupted mass balances from section 2.1 that are based on the on-land mappings and a limited region only, had to be extended. Using the correlations of marine tephras to on-shore eruptions from section 2.2, the authors in Kutterolf et al. (2008b) constructed distribution maps of the tephras that have been produced at the entire CAVA during the last 200 ka to estimate and refined more realistic erupted volumes and masses than from on-land exposures only. As a first step, the authors combined their own mapping efforts on land (Freundt et al., 2006a; Freundt et al., 2006b; Kutterolf et al., 2007a; Pérez and Freundt, 2006; Wehrmann et al., 2006) and published mapping results (CEL, 1992a, 1995a; Rose, 1987a; Wundermann, 1982; Wundermann and Rose, 1984) with their marine data from section 2.2 to construct the isopach maps of the tephra layers (Figure 7). The area covered by the investigated marine ash layers accounts for up to 10^7 km^2 in the Pacific Ocean. Although the density of off-shore thickness data per individual eruption is sometimes low and therefore the shapes of the distal isopachs and consequently the volume calculations are biased by some uncertainties, this was one of the first attempt in volcanology to determine erupted volumes

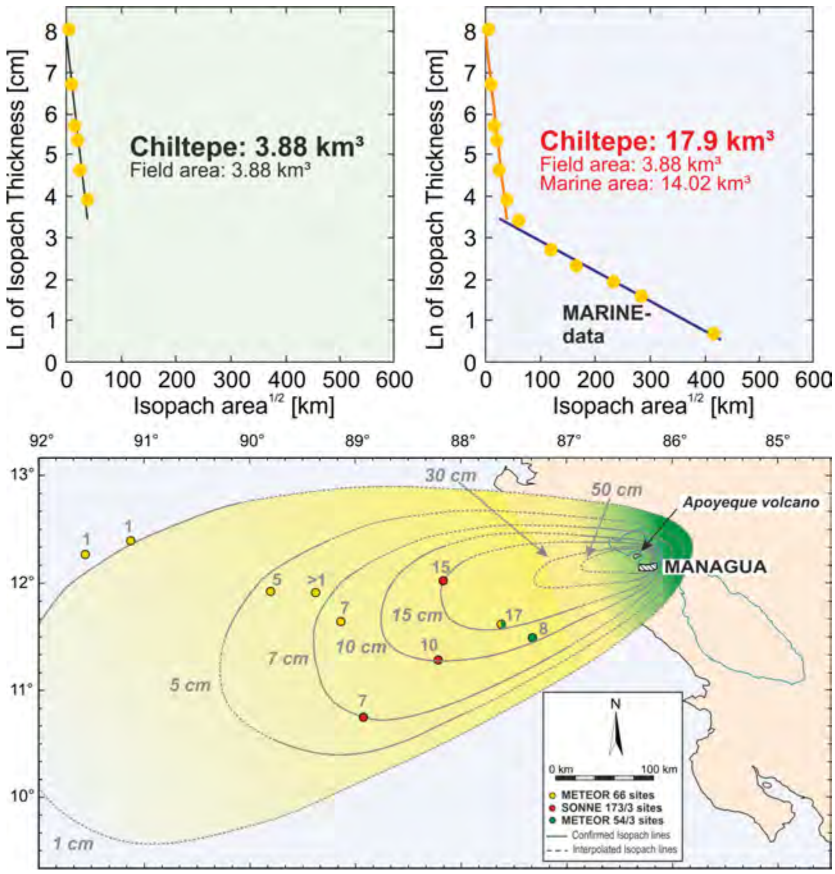


Figure 7: Lower: isopach map for the 1.9 ka old Chiletepe Tephra from Apoyeque volcanoe in Nicaragua, with isopachs on land from Kutterolf et al. (2007). Well and poorly constrained isopach sections are indicated by solid and dashed lines, respectively. Upper: Natural logarithm of isopach thickness versus square-root of isopach area for 1.9 ka old Chiletepe Tephra from Apoyeque volcanoe in Nicaragua. Proximal Chiltepe tephra data can be fitted to one line segment (upper left). Applying the method after Fierstein and Nathenson (1991) this results in a total erupted proximal onland tephra volume of ~ 3.9 km^3. Including also the distal marine thickness-distribution data (upper right), that are fitted by two line segments yield a total erupted tephra volume of ~ 17.9 km^3.

from a time series of arc-wide, highly explosive eruptions. The authors used the procedure of fitting straight lines to data on plots of ln (isopach thickness) versus square-root (isopach area) and integrating to infinity, a method introduced by Pyle (1989) and Fierstein and Nathenson (1992) that resulted in erupted volumes (Figure 7) of all major tephras along the arc that range from ~1 to 420 km^3. Initial result, that support the findings from Section 2.1, is that the distal parts of the tephra fans represent a major fraction (60-90%) of the erupted tephra volumes. To obtain the erupted masses, the proximal to medial volumes of each tephra were reduced by 50% to account for interparticle pore space (space between pumice clasts) and lithic contents. The distal marine deposits have been reduced in total by an average of ~30% (25-35% per tephra) to account for the masked ash fraction (plus 20%) in the dispersed pelagic part, directly above a marine ash layer as well as interparticle space (minus 40%) representing the space between glass shards filled with water. By including measured bulk densities per individual tephra, and distinguishing between proximal and distal locations, the volumes are recalculated to erupted magma mass. In summary, the authors showed that the widespread tephras account for 65% of the total magma output at the arc.

In a following step Kutterolf et al. (2008b) combined magma masses derived from this new tephra volumes with published volumes of the volcanic edifices (Carr et al., 1990; Carr et al., 2007). Since the compositional range of the CAVA volcanic rocks extends, due to different grade of fractional crystallization, from basalt through rhyolite, the authors also estimated the initially primitive magma masses that were necessary to produce the final amount of erupted evolved magma masses using the linear variations of increasing K_2O with silica. Finally, the resulting total magma mass produced by each CAVA volcano during its lifetime has been divided by volcano ages, to yield a long-term average magma flux at each volcano. This is still a minimum magma flux since intrusions without surface expression and losses by erosion are not accounted for. Kutterolf et al. (2008b) concluded that magma fluxes of neighbouring volcanoes are often vastly different, and peak fluxes increase northward along the CAVA. Although the magma mass fluxes suffer from a number of uncertainties (ages sometimes are poorly constrained, older tephra portions are absent due to erosion, intrusions) their values form a useful basis to calculate and approximate variations in along arc elemental fluxes of the Central American volcanic output, and estimate an overall flux budget of the Central American subduction zone. Although this is still under research and no obvious correlation to one single factor can be made in Central America (e.g. fluid flux, melting degree, slab dip, melting column height; Figure 8), the combination of different subduction parameters probably are the controlling factors for the variable magma production between arc segments and even for entire arc systems.

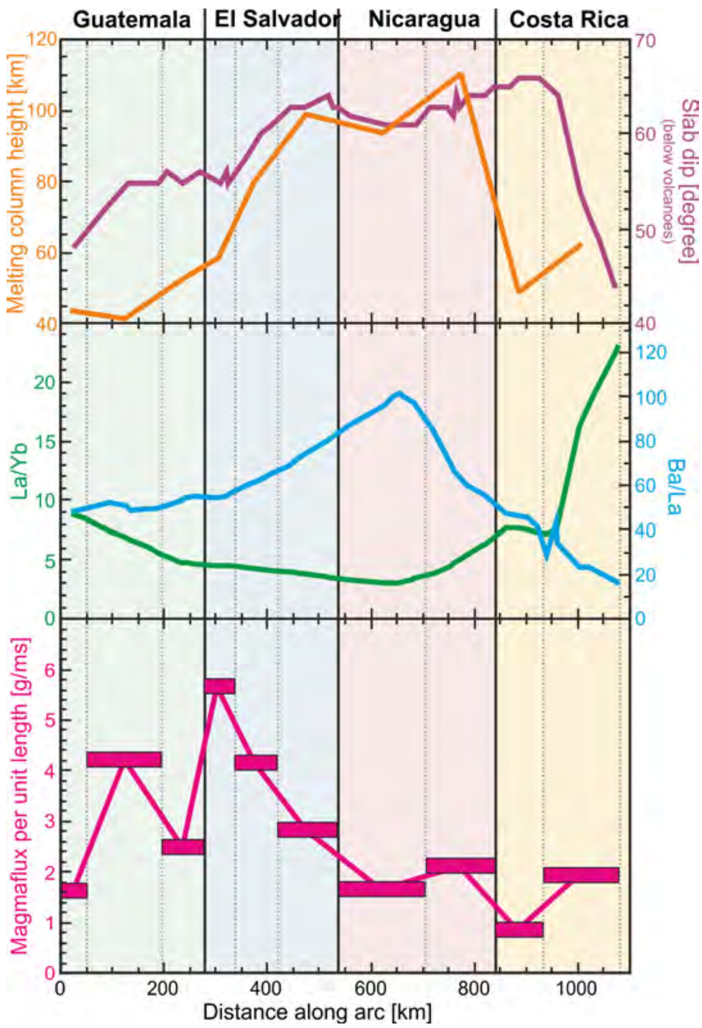


Figure 8: Long-term average magma fluxes per unit arc length for each tectonic segment of the CAVA compared with along-arc variations in geochemical and physical parameters. Ba/La and La/Yb: smoothed lines through data of Carr et al. (2007) and own data. Physical parameters are from Syracuse and Abers (2006) and Carr (1984). Melting column represents the depth below the volcanoes to the subducting slab minus lithosphere thickness.

Furthermore, regarding the entire 1100 km length of the CAVA, the total magma fluxes (including cumulates) accounts for $4.5*10^6$ g/s and accounts for an average flux per unit arc length of 4.2 g/s/m (c. $20km^3/km/Ma$ after Völker et al., 2011). Compared to estimates of global average volcanic magma fluxes, the long-term fluxes of CAVA volcanoes reach comparable magma fluxes regarding oceanic island arcs (e.g. White et al., 2006) but are slightly higher than at the Southern Volcanic zone in Chile (10 to 13 $km^3/km/Ma$, Völker et al., 2011). This discrepancy cannot be explained by the higher densities (one volcano per 13 km arc length) of smaller volcanic edifices (50 km^3) at the CAVA compared to the southern Chilean volcanic zone (24.5 km distance, 100 km^3), which compensate each other. Nevertheless, the implementation of this results in other studies, shown already in literature (Bolge et al., 2009; Kutterolf et al., sub; Metzner et al., 2012; Sadofsky et al., 2009; Völker et al., 2011), mark also the importance of tephrostratigraphy regarding further research in subduction zone budgets.

2.4 Volcaniclastic turbidites in the Miocene Shikoku Basin (IODP Expedition 322): Products of voluminous eruptions on mainland Japan

Next to the determination of eruptive masses, the source areas of unknown volcanic products are a major issue that can be addressed by using tephrostratigraphy. Just like in section 2.2 Kutterolf et al. (submitted) uses geochemical criteria to constrain the source regions of submarine deposits that are rich in volcanic matter and, like in section 2.3, assesses final volume estimates for their related eruptive events. But in contrast to the previous sections the regional focus changes to the Nankai Trough, a deep sea trench where the Philippine Sea plate subducts beneath the Eurasian Plate (~4 cm/y Seno et al., 1993). The Shikoku Basin, where the sediments from the Japanese mainland and the Izu Bonin arc have been accumulated during the last 15 Ma, contains the main lithologies being subducted now at the Nankai trough. This basin was created on the Philippine Sea plate during the Early and Middle Miocene by seafloor spreading in a back-arc setting relative to the Izu-Bonin arc system (Kobayashi et al., 1995). This region is well-known for the occurrence of large tsunamigenic mega-thrust earthquakes (Tobin and Kinoshita, 2006), and the Nankai Trough Seismogenic Zone Experiment (NanTroSEIZE) within the Integrated Ocean Drilling Program (IODP) was initiated to observe the up-dip limit of the seismogenic zone along this subduction boundary. A major goal of IODP Expedition 322 therefore, was to characterize the pre-subduction inputs of sediment and oceanic basement contributing to the seismogenic zone, by coring at two sites. These sites are located ~100 km southeast of the Kii Peninsula (Japanese mainland) and ~150–200 km west of the Izu-Bonin arc at the Kashinosaki Knoll, in the Shikoku Basin.

A major discovery of this expedition was a late Miocene (7.6 to ~9.0 Ma; Zhao et al., Submitted) interval (Unit II) of tuffaceous, volcaniclastic and normal sandstones, now named as the middle Shikoku Basin facies (Underwood et al., 2010). Based on point counting of 85 shipboard smear-slides this lithologic Unit can be divided into subunits IIa and IIb, which differ in the abundance of volcanic glass shards, mineral and/or lithic contents and bulk-rock chemical compositions. The resulting subdivision is manifested also in the exclusive occurrence of the tuffaceous sandstones (>25% pyroclasts) in the upper subunit IIa, whereas the vocaniclastic and normal sandstones appear only in subunit IIb. The upper subunit IIa consists of moderately lithified and bioturbated silty claystone including three to four 1 to 7 meter thick interbeds of tuffaceous sandstones (Figure 9).

While authors in Schindlbeck et al. (submitted) show that each tuffaceous sandstone bed derives from a single eruptive event, in this study element glass compositions of 47 samples (major elements of 47 samples with EMP and trace elements of 9 samples with laser ablation ICPMS) as well as radiogenic isotope compositions of one sample are used to constrain the provenance of the deposits. Fresh glass shards and pumice fragments that have fairly uniform major and trace element compositions in each sandstone bed can: 1) assist the interpretation by Schindlbeck et al. (submitted) that the pyroclastic material derived from different eruptive events, 2) suggest a common source region for provenance, and 3) identifies the lowermost tuffaceous sandstone (TST) bed to be different in chemical composition and therefore probably also in provenance. Fresh glass shards and pumice fragments that have fairly uniform major and trace element compositions in each sandstone bed can: 1) assist the interpretation by Schindlbeck et al. (submitted) that the pyroclastic material derived from different eruptive events, 2) suggest a common source region for provenance, and 3) identifies the lowermost tuffaceous

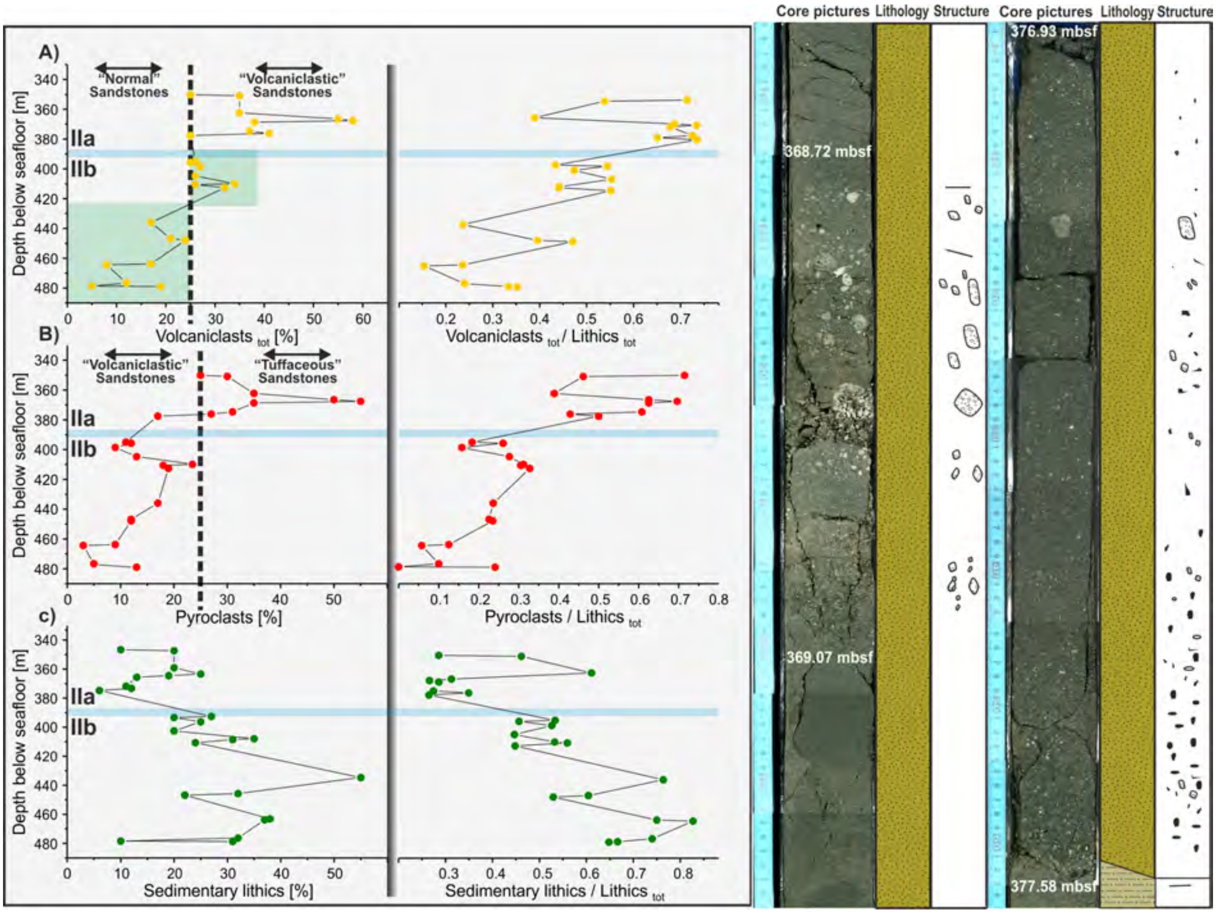


Figure 9: Left: Smear slide petrographic data for Unit II versus depth (mbsf) with the criteria for dividing into "normal", "volcanoclastic", and "tuffaceous" sandstones. On the left with total components in vol%; on the right ratios of components normalized to total lithic contents. Bluish bar represents the border between Subunit IIa and IIb. A) volcanoclastic component; vertical dashed line defines the border between "Normal" and "Volcaniclastic" sandstones after Fischer and Schmincke (1984) and green boxes, mark the difference in Subunit II between lower and upper part , B) Pyroclasts, vertical dashed line defines the border between "Volcanoclastic" and "Tuffaceous" sandstones after Fischer and Schmincke (1984); C) Sedimentary Lithics. Right: Core pictures and schematic core description for the upper most (368.72 through 369.07 mbsf) and lower most (376.93 mbsf through 377.58 mbsf) part of tuffaceous sandstone 3 showing enrichment of pumice and lithic fragments to the top and base of the sandstone bed, respectively.

sandstone (TST) bed to be different in chemical composition and therefore probably also in provenance.

Since the benefit of major element compositions for provenance analysis is limited, the authors concentrate on trace elements and their ratios, which provide better distinction between regional magmatic compositions. The first result the authors can show is that the variable trace element contents (Ba, Yb) can facilitate the initial separation into a "young" sandstone group (TST 1 to 3a) and an "old" sandstone group (volcaniclastic sandstones of Unit IIb and TST 3b), confirming the first indication that at least two, probably temporally distinguishable, source areas were tapped by the sandstones of Unit II. Furthermore, application of the Th/Yb versus Ta/Yb and Nb/Zr versus La/Sm provenance diagrams after Gorton and Schandl (2000) and Clift et al. (2003) show that pyroclast compositions of TST 1 through TST3a largely overlap with the Japanese arc field (Figure 10). The lowermost tuffaceous sandstone (TST 3b) and volcanic sandstones from Unit IIb differ by overlapping, or lying close to, the Izu Bonin data fields.

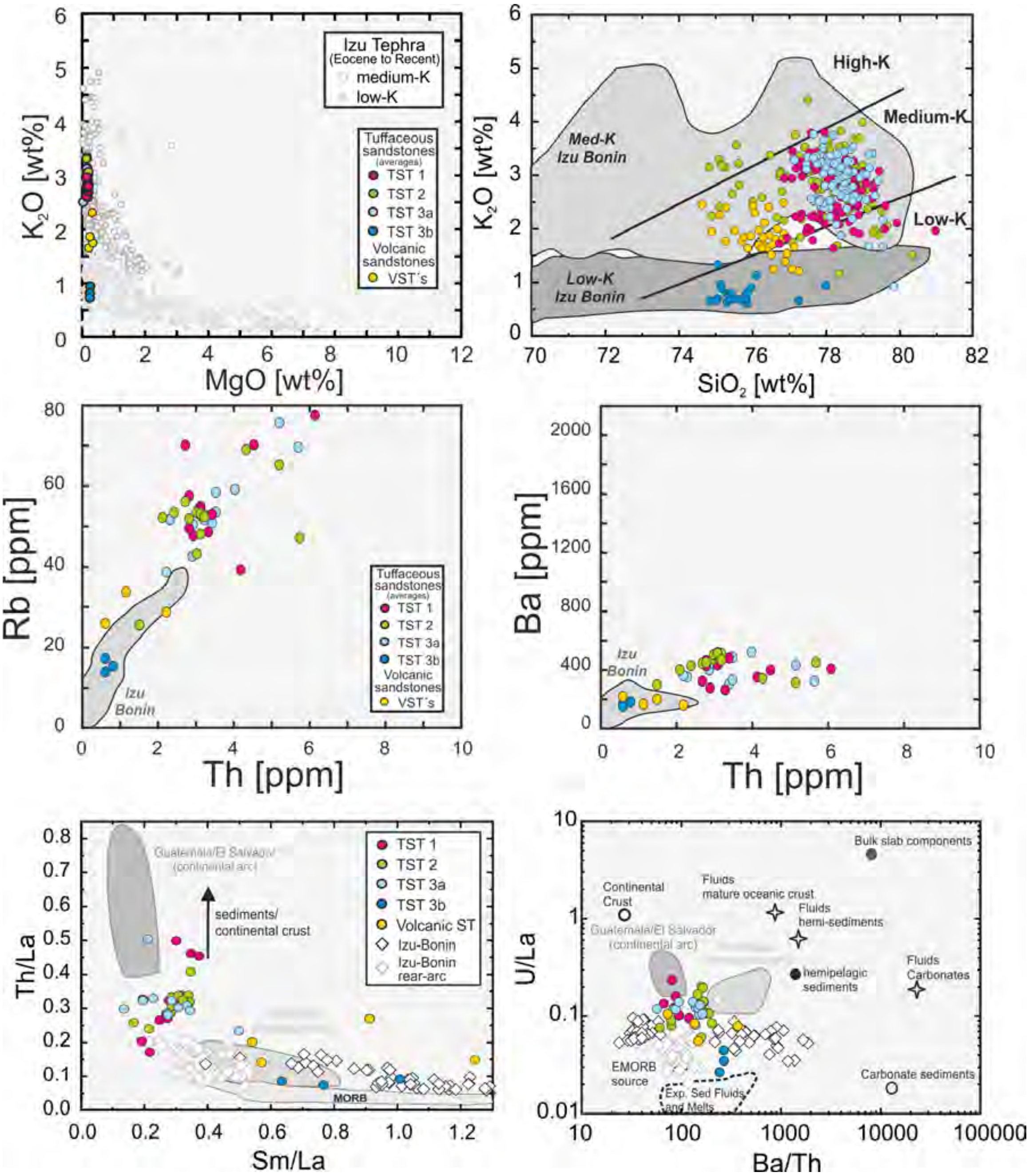


Figure 10: Major (K_2O versus MgO; SiO_2 versus K_2O) and trace (Th versus Rb, Ba) element discrimination diagrams, from glass shards analysis of tuffaceous sandstone 1 to 3 and volcanic sandstones of Unit IIb in comparison to data from pumices in submarine mass flows from Izu-Bonin arc and back arc are shown (grey fields) and complemented by highly differentiated medium-K samples from Izu-Bonin Arc and backarc (Nishimura et al., 1992; Straub, 1995, 1997; Straub, 2002; Straub et al., 2010; Straub and Layne, 2003; Straub et al., 2004). Trace element ratio diagrams from literature (Bryant et al., 2003; Patino et al., 2000) indicating different influences to source areas by continental crust interaction or a sediment signal from the slab in comparison to the analyzed tuffaceous sandstones of this study. Data from the original authors are complemented by data from Izu Bonin arc (black diamonds) and rear arc tephras (grey diamonds Clift et al., 2003; Kimura et al., 2002; Kobayashi and Nakamura, 2001; Shibata and Nakamura, 1997; Straub and Layne, 2003; Tatsumi, 2006; Tatsumi et al., 2008; Togashi et al., 1992; Ujike and Stix, 2000). Additionally compositional fields from the Central American Volcanic Arc are included (Kutterolf et al. sub) showing oceanic (Nicaragua; light grey) to continental (Guatemala; dark grey) crustal influence.

Additionally, elevated values of Th/La, La/Sm, Rb/Hf or Th/Nb for TST 1 to TST 3a suggest an influence of continental crust or subducted terrigeneous sediment on magmatic compositions (e.g. Bryant et al., 2003; Vogel et al., 2006), whereas elevated values of U/Th at low Th/Nb in TST 3a, as well as in the volcaniclastic sandstones of Unit IIb, indicate an influence of pelagic sediment-derived fluids on the Izu Bonin magmatic compositions (cf. Straub and Layne, 2003)(Figure 10). In contrast to the Japanese mainland (Isozaki et al., 2010), there is neither continental crust nor trench sediment of continental composition at the Izu-Bonin arc, which is not a likely source region for the tuffaceous sandstone beds above TST 3b. Since both, TST 3a and TST 3b, have the same grain sizes and lithological structures, the authors further conclude that both sandstone beds seem to have distances in the same order of magnitude to their sources. The authors favor an origin in the former area of the Izu Peninsula (on today's Japanese mainland), as the collision zone between Izu arc and the Japanese paleo-arc, since here both geochemical signatures were available in the late Miocene. This is additionally supported by isotope data of a pumice fragment from TST1, that clearly differs from the Izu-Bonin isotope compositions, but equals the isotope ratios for the modern Zao and Fuji volcanoes (Gust et al., 1997; Nakamura et al., 2008; Watanabe et al., 2006) that are part of the volcanic front in the vicinity of Izu Peninsula. To use again tephrostratigraphy for quantification of erupted volumes, the authors estimated the sheet-like distribution area (Zenisu-daiichi Fan after Pickering et al., submitted) of the tuffaceous sandstones in the Miocene between the plausible source region and the 400 km distant Site 322, using bathymetric and seismic constraints after Pickering et al. (Pickering et al., submitted). Including an approximated thickness decay per sandstone bed, the authors calculated minimum erupted magma volumes between ~1 km^3 to 17 km^3 dense rock equivalent (DRE) for the individual sandstone beds. Finally, the authors conclude that a series of large volume eruptions occurred during the Late Miocene time at the Japanese continental margin, most probably associated with the initial collision (7.8 to 8.3 Ma) of the Izu-Bonin arc with the Japanese paleo-arc.

2.5 Pacific offshore record of plinian arc volcanism in Central America: 3. Application to forearc geology

Next to the previously shown tasks of tephrostratigraphy for volume estimates in volcanology, chronostratigraphic application affects, for example, the identification of processes in the forearc regions of subduction zones as well as its temporal variability. In Kutterolf et al. (2008c) the authors summarized the benefit that their studies of sections 2.1, 2.2, and 2.3 had regarding the research of the Central American forearc geology. The ash layers correlated with 26 known eruptions on land in Kutterolf et al. (2008a) provide absolute time lines through the marine sediment successions across the entire Central American Trench region. By using this marker beds, geological processes on the subduction erosion affected Pacific forearc can be unravelled temporally. In particular, sediments of the continental slope as well as structures within (submarine landslides) and on top (fluid venting sides) benefit from this application of tephrostratigraphy. The authors emphasized in their manuscript that such temporal constraints are essential to understand the dynamic processes, and to identify forcing mechanisms and external controls, for slope features.

With time marks that are constrained by bracketing tephras of known age, average apparent sedimentation rates of the intercalated pelagic sediment can be calculate (Figure 6). One result is, for instance, that on the incoming plate offshore Central America the accumulation rates of pelagic sediment range between c. 1–6 cm/ka, whereas for the continental slope the normal sedimentation rates are much higher (30-40 cm/ka). Nevertheless, time intervals can be identified where the apparent pelagic sedimentation rates significantly vary laterally on the forearc and on the incoming plate. A period of unsteadiness at 17-25 ka on the forearc, for example, identified periods of erosion and enhanced accumulation on the slope, probably caused by climatic and/or tectonic conditions on land. On the other hand, unsteady conditions on the incoming plate, manifested by extremely low apparent sedimentation rates at time intervals >50-80 ka, are not common but probably indicate stronger tectonic activity in this time interval than during younger times. In turn, this suggests bend-faulting across the outer rise to be unsteady on longer time scales, triggering erosion and re-sedimentation.

Additionally, the geotectonic setting of the Central American Fore arc, with its fast erosive subduction of the rough Cocos Plate beneath the Caribbean Plate, leads to an over steepening of the Nicaraguan continental slope (Ranero et al., 2000; von Huene et al., 2003). This favoured the instability of the slope sediments and the possible collapse as submarine landslides (Harders et al., 2010; Harders et al., 2011). Offshore Nicaragua the tephra layers within the slide sediments or at the slide scarps constrained ages of >60 ka, c.19 ka and <6 ka, for three larger landslides at the continental slope. Intercalated ash layers, however, not only constrain the times at which submarine landslides detached from the continental slope, they are often associated with low-strength shear planes when ash layers are forming structurally weak zones used for detachment (e.g. Harders et al., 2010; Harders et al., 2011). In particular Kutterolf et al. (2008c) showed that, for example, the mafic ash layer in the detachment zone of the Hermosa slide can be correlated with the c. 6 ka old San Antonio Tephra, erupted from Masaya Caldera (Kutterolf et al., 2007a; Perez, 2007). Next to the consequent result that the slide detachment occurred less than 6 ka ago, grain size variability within the ash layer indicates a connection between preferential detachment plane and a certain grain size spectrum (Figure 11) showing probably a connection between the loss of the 125 to 250 µm fraction and the horizon in the ash layer where the slide has been initiated.

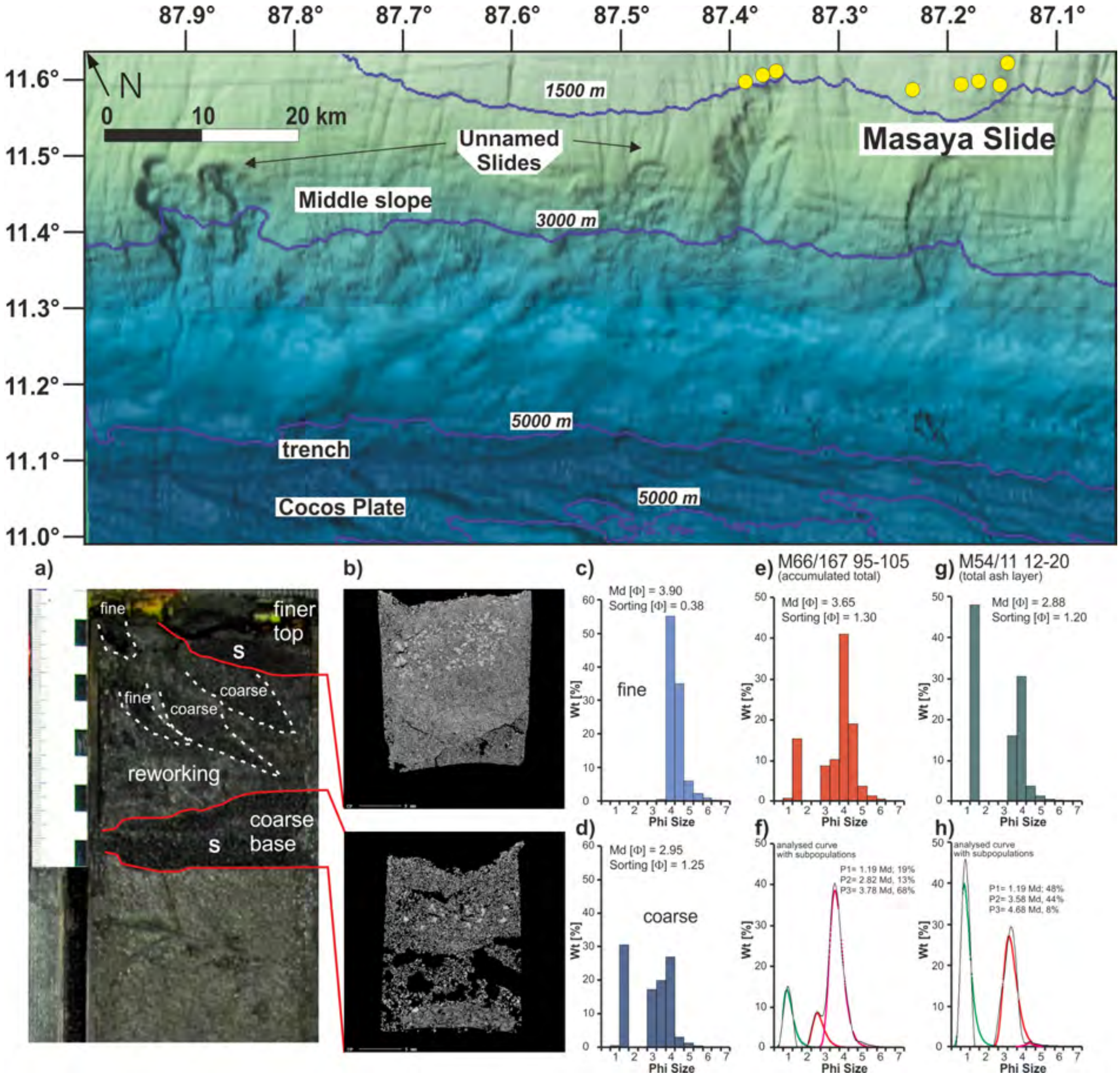


Figure 11: Upper: Bathymetric map of the Central Nicaraguan Slope with the major submarine slide scars. Lower: A) Photograph of San Antonio ash layer in core M66/167 95-105 with coarse base and finer top and the displaced partly reworked middle part comprising several lenses of the upper and lower part. S= sample location for grain size analyses. b) Backscatter electron microprobe pictures showing the coarse and cage like structure of the lower and the finer more massive , more impermeable upper part of the ash layer M66/167. c) grain size distribution histogram of the finer upper part of ash layer M66/167 (grain sizes in φ-classes). d) grain size distribution histogram of the coarser lower part of ash layer M66/167 (grain sizes in φ-classes). e) grain size distribution histogram of the accumulated data set of both, upper and lower, parts of the ash layer M66/167 (grain sizes in φ-classes). f) Smoothed grain size distribution curve with modelled subpopulations for M66/167. g) grain size distribution histogram of the comparison ash layer M54/11 12-20. h) Smoothed grain size distribution curve with modelled subpopulations for M54/11. Grain size analyses and modelling have been conducted with the program Kware SFT of K. Wohletz (2007).

Using intercalated ash layers, Kutterolf et al. (2008c) also exemplarily determined the durations of highly active periods in the multi-stage growth history of mud mounds offshore Central America, which is discussed in more detail in the next section.

2.6 Lifetime and cyclicity of fluid venting at forearc mound structures determined by tephrostratigraphy and radiometric dating of authigenic carbonates

The classical purpose of marine tephrostratigraphy, where ash layers act as marker beds in marine sediments, is summarized in the first part of Kutterolf et al. (2008d). The correlation of widespread ash layers to well dated plinian eruptions at the Central American Volcanic Arc (sections 2.1 and 2.2) is used to date numerous sites of fluid venting and mud extrusions, localized and identified by high resolution bathymetric methods, seismic profiling, and video records at the Central American forearc (Bohrmann et al., 2002; Grevemeyer et al., 2004; Hensen et al., 2004; Mau et al., 2006; Moerz et al., 2005; Ranero et al., 2008; Talukder et al., 2007)(Figure 12).

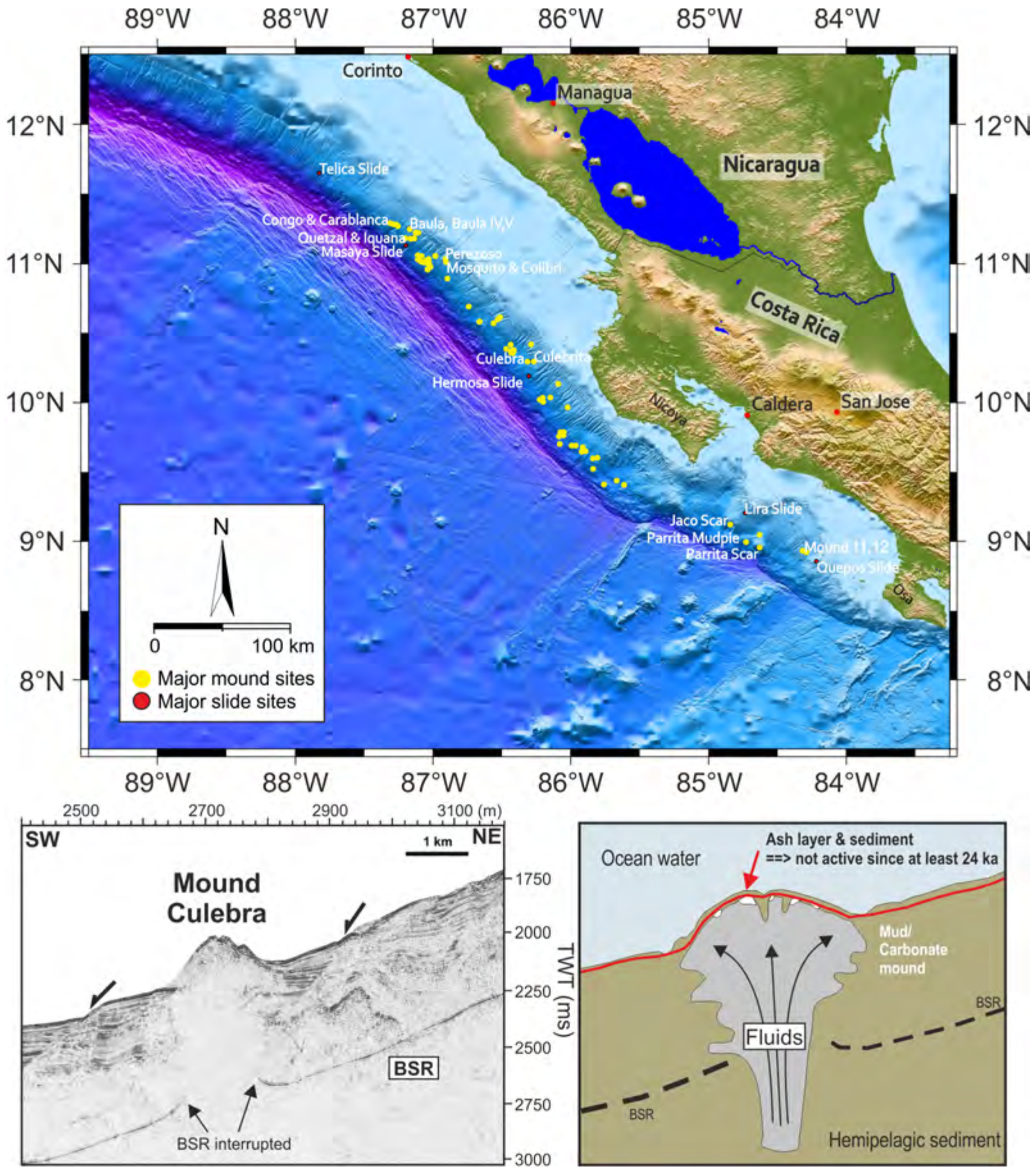


Figure 12: Upper: Shaded and colored Shuttle Radar Topography Mission (SRTM) elevation model of Central America with high-resolution bathymetry of the Middle American Trench. Yellow dots mark fluid venting structures mapped by Ranero et al. (2008), red circles represents major slide scars. Lower left: Migrated seismic profile (multichannel seismic reflection [MCS] Line GeoB 02-430, modified after Moerz et al., 2005) across Mound Culebra and adjacent smaller venting structures. Note irregular shape of bottom-simulating reflector (BSR) and lack of seismic energy beneath the mound. Up-bended sediment strata suggest diapiric ascent inside Mound Culebra. Lower right: Schematic cross section of a mound structure with carbonate caps overlain by an ash layer. BSR marks the base of hydrate layer interrupted by mud diapirism.

In general, fluids rise through the forearc at convergent margins in response to upper plate consolidation and dewatering of the subducting plate. When the fluids escape at the seafloor they produce various cold seep related features on the seafloor (mud diapirs, mud mounds) and authigenic carbonates precipitate from rising fluids within such structures during active venting (Figure 12). This activity produces typically mixed or unimodal mud/carbonate clast debris on the surrounding seafloor, where it became intercalated with normal pelagic background sediments and indicate directly changes in the activity status of the fluid venting structure (Figure 13). Kutterolf et al. (2008d) used the occurrence of this debris in the normal background sedimentation of the slope, together with the intercalated ash layers that provide time marks, to constrain, for the first time, the ages of mud-ejection activity or enhanced carbonate growth at an entire forearc region.

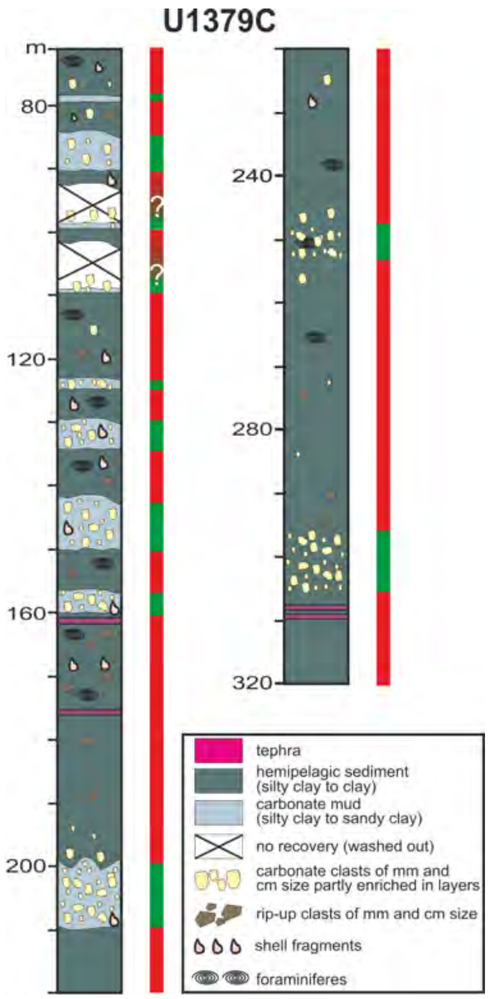


Figure 13: Selected lithology section of IODP Expedition 334, Site U1379 Hole C, 70 mbsf through 320 mbsf with ash layers representing time markers within the alternating clast-rich carbonate mud (green bars) and hemipelagic sediment (red bars)(Expedition 334, cruise report). Future investigations will show how the timing of this extensive sequence can extend the model of Kutterolf et al. 2008e with multiple active and passive fluid venting phases restricted to one location.

Multiple ages, derived from tephra layers at each of the ten investigated fluid venting locations (Mounds Congo, Carablanca, Baula, Iguana, Perezoso, Colibri, Culebra and Mounds 10, 11, and 12), indicated the activity stages along 450 km of the continental slope offshore Nicaragua and Costa Rica within the last 322 ka (Figure 14). Additionally the authors complemented these age constraints by ^{14}C and U/Th dating of wood fragments from the pelagic sediments and carbonate samples taken in stratigraphic order from up to 3 m long drill cores of carbonate caps, respectively. Radiometric dating constrained active phases at 8.3 and 5.6 ka for Mound Baula, 65.6 and 32.1 ka for Mound Iguana as well as 70.3 and 55.8 ka for Mound Perezoso offshore Nicaragua and 16.8 ka, 42.5 ka and 46.4 ka for Mound 10, ~3 ka to at least ~9 ka for Mound 11, and 10.1 ka, 19.4 ka, and 22.6 ka for Mound 12 offshore Costa Rica (Figure 14). These ages overlapped largely with periods of mud extrusion derived from ash-layer ages.

Together, all age constraints at the fluid venting structures revealed that Mound 11, offshore Costa Rica, is entirely composed of deposits that suggest continuous activity for >10 ka. In contrast, Mound Culebra (offshore Nicoya peninsula, Costa Rica) contains the oldest sediments (322 ka) that are characteristic for active venting phase but has been inactive for at least 100ka, although observations by Mau et al. (2006) indicate recent resurgence of venting activity. Kutterolf et al. (2008d) also shows that the lifetime of cold seeps generally can exceed 100 ka, which is shown at the Nicaraguan mounds Carablanca, Iguana and Colibri. Recent activity in the sediments had only been found at Mounds Baula (Nicaragua) and 10 (Costa Rica), starting c.

30 ka ago whereas at Mounds Congo, Carablanca, Perezoso (Nicaragua) and Mound 12 (Costa Rica) the most recent fluid venting phase ended 10–15 ka ago. Additionally, multistage activity can be assumed for Mounds Colibri (Nicaragua) and Mound 10 (Costa Rica), which had three active phases in the last 100 ka; however, a decrease in activity coincides at ~7 ka at both locations. At least two active periods of increased activity occurred at Mound Iguana (Nicaragua) at 15–30 and at >50 ka.

In summary, the results indicate two principal types of mound structures co-existing next to each other that are characterized 1) by a monogenetic, long-living mound type, and 2) a multiphase mound type with high activity periods lasting 10–50 ka that alternate with >10 ka intervals of low activity. The results also have shown that active and inactive phases of fluid venting can occur simultaneously at mounds lying close to each other (Figure 14).

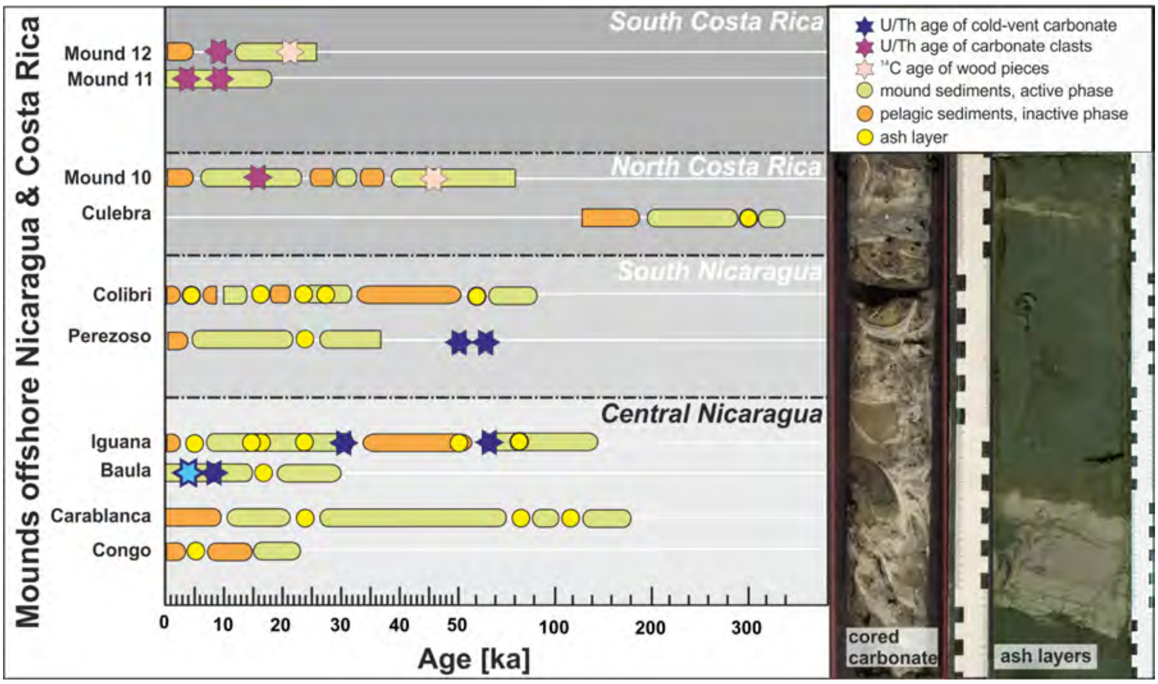


Figure 14: Ages of sediment packages generated during active venting (light green bars) and of intervals of pelagic background sedimentation (orange bars) constrained by dated ash layers (yellow dots) in cores next to mound structures. Colored stars indicate ages of authigenic carbonate cements, carbonate clasts, and wood pieces, which overlap with active periods. Note changing scale on age axis at 50 ka. Representative picture of ash layers (0.59 to 0.61 mbsf and 0.86 to 0.96 mbsf) from expedition M54/2 core 11 and form a cored carbonate with British Geological Servey (BGS) rock drill device from expedition M66/3 core 215.

Furthermore, Kutterolf et al. (2008d) also found phases in the past where the bulk of the mound structures had eventually been simultaneously active (~20–25 ka; >50 ka), suggesting a more regional or even global controlling factor on the fluid venting activity. The authors proposed that strong sea level decreases (cf. Lisiecki and Raymo, 2005) correlating with this time periods, to be responsible for these scenarios, since this could possibly induce regional or even global stress changes in the hydrological system at the continental slopes and favour enhanced fluid flow (cf. Hensen et al., 2004; Teichert et al., 2003). The authors also suggests regional tectonic changes as another possible trigger mechanism for increased fluid venting activity at the mound structures of the Nicaraguan continental slope (cf. Vannucchi et al., 2003). In summary, the authors provided first and continuous data on the lifetime and cyclicity of cold seeps from a large forearc area (450 km). These results will affect future forearc studies regarding biogeochemical processes, the hydrological forearc system, carbonate precipitation reactions and mound formation in response to tectonic and/or climate changes.

2.7 A detection of Milankovitch frequencies in global volcanic activity

Since volcanic activity seems to vary in a cyclic manner over a wide range of temporal scales (<1 year to 10^6 years; Cambray and Cadet, 1994; Kennett et al., 1977; Mason et al., 2004; Paterne et al., 1990), researchers are searching for connections between volcanism and global acting geological cycles to unravel the possible processes behind this periodic occurrence of volcanism.

The new established marine tephrostratigraphy offshore Central America (Kutterolf et al., 2008a; Kutterolf et al., 2007a), which provides an almost complete record of explosive volcanism, inspired the authors, very early on, to search for cyclic pattern in the ash layer record. In a first preliminary statistical analysis they determined frequency distributions over time, and yielded a period of low ash layer abundance between 120 to 160 ka and, in turn, evidences for abundant Plinian eruptions during the periods 0-120 ka and 160-280 ka (Figure 15). This preliminary data from Central America already indicated eruptive activity evolving in cycles with periods in order of 10^5 years, the range of the climate induced Milankovitch cycles.

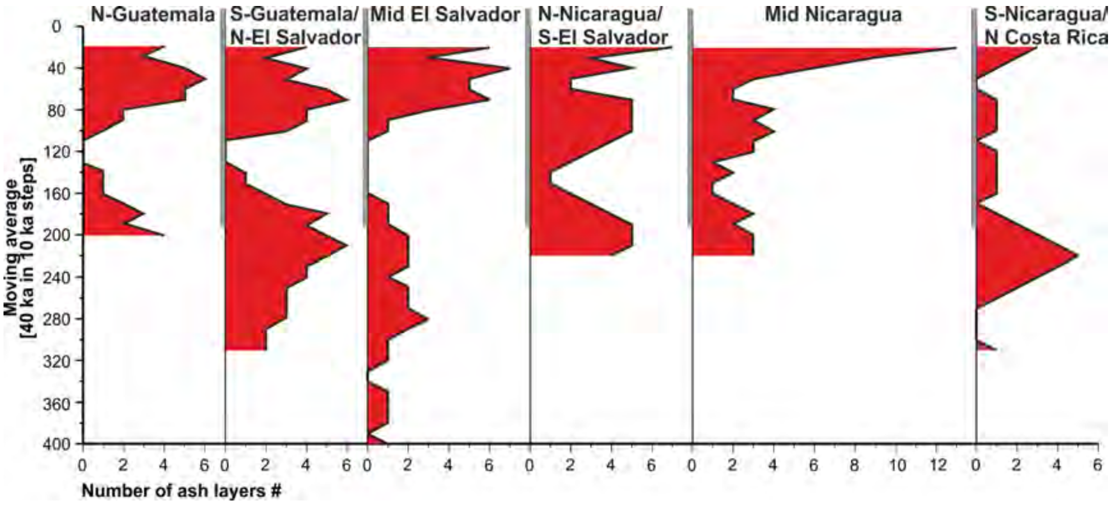


Figure 15: Frequency versus age diagram of 6 regions along the CAVA from the North of Guatemala to the North of Costa Rica (From North to South: North Guatemala, South Guatemala/North El Salvador, Middle El Salvador, South El Salvador/North Nicaragua, Middle Nicaragua, South Nicaragua/North Costa Rica) using a moving average (40 ka time window) of ash abundance in the cores along the arc at each site location.

Although connections between tectonics, the global carbon cycle and climate appear to be well established at longer timescales (Walker et al., 1981) and volcanic eruptions are known to influence climate on shorter time scales, (e.g., Hansen et al., 1992; Robock, 2000) and perhaps vice-versa at regional scales (Jellinek et al., 2004; McGuire et al., 1997; Novell et al., 2006; Rampino et al., 1979), a general link between glacial cycles and global volcanic activity has remained elusive.

The next logical step was to extend the data set to other subduction regions on Earth and to the past (1 Ma) to evaluate if these observations are locally limited or can be assigned also to regional or even global areas. The manuscript Kutterolf et al. (2012) analyzed, additionally to the CAVA data, marine tephra records at DSDP/ODP/IODP drill sites within 200–500 km from their respective sources at the ROF (Figure 1). Whereas the marine tephra records from Central America and, partly, New Zealand are dated using estimated sedimentation rates and/or through correlation with radiometrically dated on-land deposits (Kutterolf et al., 2008a), the tephras found in the remaining cores from the Ocean Drilling Programs are exclusively dated by using estimated sedimentation rates. In total, 408 tephra layers at sites along the ROF have been identified and dated with age uncertainties better than 14%. After converting the tephra data set into a binary time series, a stable-phase running average low-pass filter has been applied to the time series with a window width of 5 kyr. This is followed by a multi taper spectral analysis (Percival and Walden, 1998; Thomson, 1982) resulting in a noisy major frequency peak of 1/44 kyr as well as subordinate periodicities around 1/100 kyr and 1/23 kyr in the power spectra (Figure 16). To identify the time dependence of the data set, the authors repeated the same analysis on a sequence of overlapping 400 kyr windows centered at progressively increasing ages (Figure 16). This resulted in a clear peak at a frequency of 1/41 kyr, the Milankovitch obliquity frequency, which can be identified for the most recent segment and which spans 0-400 ka. The amplitude and center frequency of this peak, however, tends to decrease with age in the following analyzed time segments (Figure 16), possibly because of timing errors that lead to distortion of the spectral estimate (Huybers and Wunsch, 2004). Nevertheless in each case considered in Figure 16 this peak remains statistically significant. This is assisted by a significance study of the peak nearest to obliquity. Using the data set, a search for the most pronounced frequency peak within +/-14%, the range of dating errors, of the 1/41 kyr obliquity frequency has been conducted and resulted in the highest significance at the identified 1/44 kyr peak (6.3 times than the background continuum). To exclude the possibility of an accidental frequency peak in the ash record, a series of 100,000 synthetic time series have been build and analyzed with randomly varying time constraints in the order of the 14% error at each used tephra event. Frequency analyses conducted again over all synthetic time series reveal 99% of probability that the periodicities in the used ROF tephra time series and its significance of 6.3 over the background level at 1/44 kyr cannot be achieved by accident.

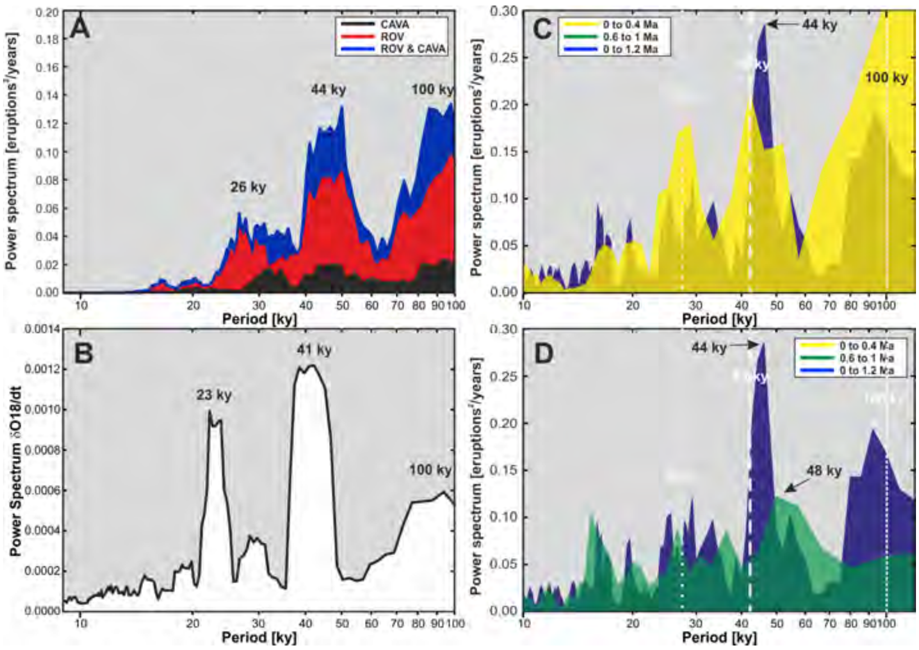


Figure 16: A) Power spectra of the tephra layer records for the unturned ROV, CAVA, and ROV&CAVA time series. Power spectra, computed with a time-bandwidth of 1.5, have been normalized to the maximum value in the 40–50 ky band to allow better comparison. Major orbital periodicities can be recognized. B) Power spectra of the time rate of change of a Pleistocene stack of δ^{18}O records (Lisiecki and Raymo, 2005) indicating the typical Milankovitch frequencies with emphasize on the obliquity 41 kyr bandwidth. C) + D) Power spectra of the ash time series filtered with a stable phase running average low pass filter (window length 5 k.y.). Individual spectra with are generated for different time windows (width of 400 k.y.) centered at 200 k.y and 800 k.y. Blue line denotes power spectra of the entire record. The subsets exhibit a slight decrease in peak frequency and amplitude at the obliquity band with increasing age. The decrease with time is attributed to systematic errors such as the overestimation of ages for older samples and decreasing number of samples populating older subsets.

As a result and to further evaluate the

obliquity-related spectral peak, the ash time series has been compressed by a factor of 10%, which also compensated the largest error effect on the absolute ages of the oldest samples, for which uncertainties are the largest. Additionally, the presence of less intense 1/100 kyr and 1/23 kyr frequencies in the spectrum, although with lower significance, is in accordance with other indicators of late Pleistocene climate and confirms a connection between variations in climate and volcanism during the last Million years.

Furthermore the results strongly suggest that climate variations producing glacial cycles also induce volcanism, and that the physical link may be the changes in crustal stress associated with changes in surface mass loading (ice/ocean) and the associated isostatic adjustment of the solid Earth (Glazner et al., 1999; Huybers and Langmuir, 2009; Jull and McKenzie, 1996; McGuire et al., 1997; Sigvaldason et al., 1992). This loading mechanism is further supported by an observed phase relationship within the 41 kyr obliquity band. The occurrence of increased volcanism slightly lags behind the highest rate of increasing eustatic sea level (Lisiecki and Raymo, 2005), by 4.0 ± 3.6 kyr and can be compared to the regional study of Jellinek et al. (2004) in Eastern California, where volcanism lagged behind glacial unloading by 3.2 ± 4.2 kyr.

Furthermore, applying numerical models for global changes in normal stress during deglaciation after Wu and Peltier (1982) resulted in a map that shows the rate of change of radial stress at 10ka, for example, during the final deglaciation phase of the ice age, at a depth of 20 km (Figure 17). Subsequently the authors compared the rate of change in radial stress below the CAVA with its eruption time series of the last glacial cycle, which yielded 1) a correlation between the highest rate of stress and the highest amount of eruptions in the last 20 ka, and 2) an additional support for the causal link between variations in ice age climate, continental stress field, and volcanism. The authors concluded that a more fundamental goal of future work would be the quantification of a possible feedback loop between climate, volcanic output and continental stress field.

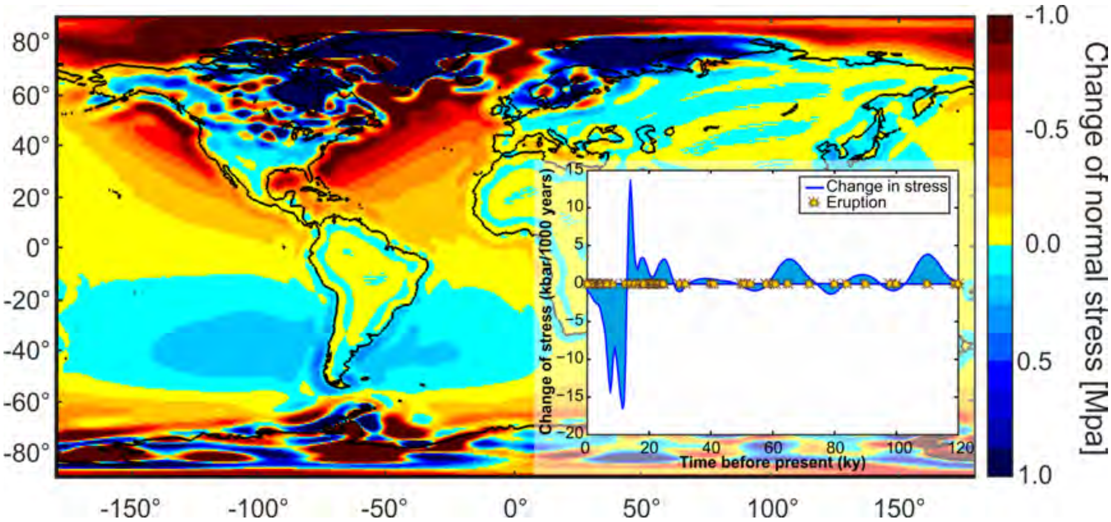
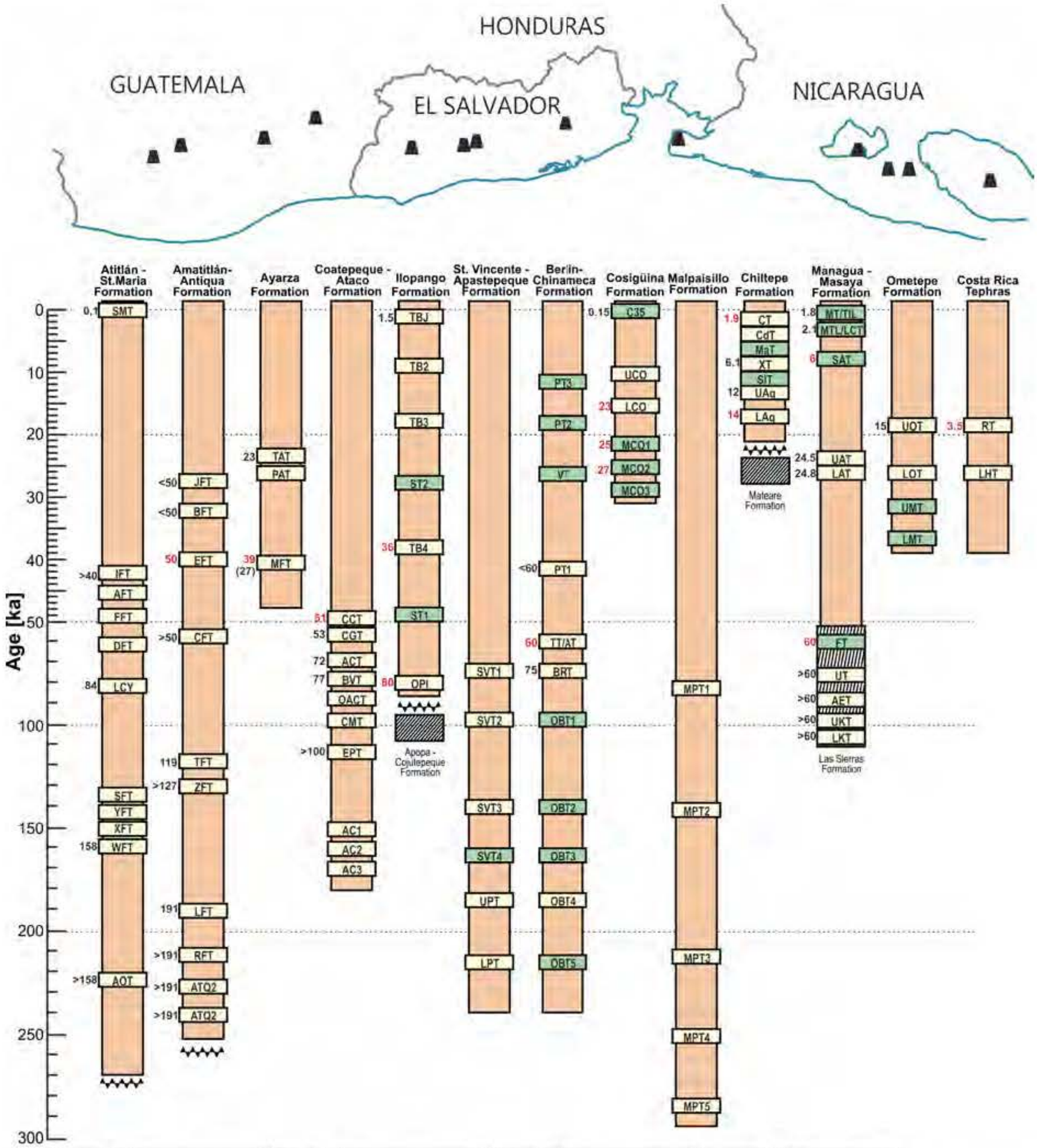


Figure 17: Numerical prediction of the ice age induced rate of change of normal stress at 20 km depth (units of MPa/10kyr) and at 10 ka (i.e., during the final deglaciation phase). Inset: Predicted rate of change of normal stress at 20 km depth below the CAVA core site (Figure 1) across the last glacial cycle (blue line). Data for older glacial cycles are not sufficient to compile a correct stress model. The yellow dots indicate the age of tephra layers identified in the CAVA sedimentary gravity core. For details of the Earth model and ice history used in this numerical calculation see Kutterolf et al. (2012).

3. Conclusion

Overall, this thesis shows how important modern tephrostratigraphy is to unravel geological mysteries, especially in geological settings where other time markers are rare or missing. This thesis was focused on the marine realm at subduction zones, but also emphasizes that the integrative research of on-land tephra records with offshore tephras represents a real strength in modern tephrostratigraphy and provides tools for 1) dating of marine ash layers by correlation with dated tephras on land, resulting also in more precise local to regional sedimentation rates, 2) the determination of more reliable eruption parameters by integrating the distal depositional areas of large eruptions, 3) extending the tephrostratigraphy of volcanic complexes and entire regions much further to the past, favoring also a better and more reliable eruptive history, 4) the determination of time constraints for slope processes, including mass wasting events and fluid venting periods, and, 5) unraveling global relationships between explosive volcanism and climate changes or vice versa. Large parts of this thesis are focused on the Central American subduction zone and therefore the completely revised tephrostratigraphy (Figure 19) for the whole Central American Volcanic Arc, identifying also the connections between isolated volcanic complexes along the entire arc, is one of the major scientific outcomes of this work, which will potentially have impact also for public issues like hazard assessment and road and house building in the next decades.

Figure 18: Simplified composite stratigraphic successions of known Late Pleistocene/Holocene tephras from highly explosive eruptions in Central America (modified from Kutterolf et al. 2008b). Yellow bars mark silicic tephras, and green bars mafic tephras, respectively. Major unconformities in the successions are shown by black zigzag bands. Individual numbers in red next to tephra layers mark absolute ages by radiometric age dating using 14C, K/Ar or Ar/Ar, whereas estimated ages from pelagic sedimentation rates after Kutterolf et al. (2008c) are given in black.



Acronym	Tephra	Acronym	Tephra	Acronym	Tephra	Acronym	Tephra
LHT	Laguna Haule Tephra	CdT	Los Cedros Tephra	UPT	Upper Apastepeque Tephra	BFT	B-Fall Tephra
RT	Rincon Tephra	MaT	Mateare Tephra	LPT	Lower Apastepeque Tephra	CFT	C-Fall Tephra
UOT	Upper Ometepe Tephra	XT	Xiloa Tephra	TBJ	Terra Blanca Joven	TFT	T-Fall/Flow Tephra
LOT	Lower Ometepe Tephra	SIT	San Isidro Tephra	TB2-4	Terra Blanca 2 to 4	ZFT	Z-Falls Tephra
UMT	Upper Maderas Tephra	Uaq	Upper Apoyeque tephra	OPI	Old Pomice Ilopango	LFT	L-Fall/Flow Tephra
LMT	Lower Maderas tephra	Laq	Lower Apoyeque tephra	CCT	Conacaste Tephra	RFT	R-Falls/Flow
MT	Masaya Tuff	MPT1-5	Malpaisillo Tephras 1-5	CGT	Congo Tephra	SMT	Santa Maria 1902
MTL	Masaya Triple Layer	C35	Cosigüina Tephra 1835	ACT	Arce Tephra	IFT	I-Falls Tephra
SAT	San Antonio Tephra	UCO	Upper Cosigüina Tephra	BVT	Bella Vista tephra	AFT	A-Fall Tephra
UAT	Upper Apoyo Tephra	LCO	Lower Cosigüina Tephra	OACT	Old Arce Tephra	FFT	F-Fall Tephra
LAT	Lower Apoyo Tephra	MCO1-3	Mafic Cosigüina Tephras 1-3	CMT	Cilamatal Tephra (IG)	DFT	D-Fall Tephra
FT	Fontana tephra	PT1-3	Pacayal Tephras 1-3	EPT	Empalisada tephra	LCY	Los Chocoyos
UT	Unicit tephra	VT	Vulkan Tephra	AC1-3	Ataco Tephras 1-3	SFT	S-Fall Tephra
AET	Archaeo Apoyo Tephra	TT/AT	Twins Tephra/A-Tephra	TAT	Tapalapa Ash Tephra	YFT	Y-Fall Tephra
UKT	Upper Krypto Apoyo tephra	BRT	Blanca Rossa tephra	PAT	Pinos Altos tephra	XFT	X-Fall Tephra
LKT	Lower Krypto Apoyo tephra	OBT1-5	Old Berlin Tephras 1-5	MFT	Mixta Fall Tephra	WFT	W-Fall/Flow Tephra
CT	Chiltepe Tephra	SVT1-4	San Vincente Tephras 1-4	JFT	J-Fal Tephra	AOT	Atitlan older Tephra

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Danksagung

Die vorliegende Habilitation entstand im Zuge des SFB574 an der Christian-Albrechts Universität zu Kiel und auf Anregung von Herrn PD Dr. **Armin Freundt**.

Deshalb gebührt ihm auch mit der größte Dank, denn er hat mich während meiner 11 Jahre nach der Dissertation immer begleitet, immer unterstützt und war in jeglichen Lebenslagen für mich da als Chef, Kollege und Freund. Ich vermisse die fruchtbaren, erfolgreichen, lehreichen und so eindrücklichen gemeinsamen Expedition nach Lateinamerika und wünsche mir nichts sehnlicher als deren Fortsetzung; Immer tranquillo und Cuba Libre :-).

Herrn Prof. **Kaj Hoernle** gebührt ein ähnlich großer Dank, denn auch er war ein tatkräftiger Unterstützer während meiner ganzen Zeit im SFB574 und hat sich auch immer trotz Zeitmangel für meine Belange eingesetzt.

Natürlich möchte ich mich auch bei meiner **Habilitationskommission** bedanken die bereit sind diese Aufgabe zu übernehmen.

Ein besonderer Dank geht an alle Leutchen im **SFB 574** für die tolle und wissenschaftlich fruchtbringende Zeit die wir in allen Phasen miteinander haben konnten und die mir persönlich einen deutlich breiteren Blickwinkel für Geowissenschaften gebracht hat.

Natürlich ohne euch liebe **Co-Autoren** würde es gar nicht gehen! Deshalb nochmals an dieser Stelle einen herzlichen Dank für die vielen gemeinsamen Momente während der Land- und Schiffsexpeditionen, der Messungen in Laboratorien und den vielen Diskussion über E-Mails oder auch direkt während der Erstellung der Manuskripte. Und natürlich auch ein großes Dankeschön an alle **Techniker** zu Land, Wasser und Luft, in den Laboren, an den Computern und auf Deck. Und ganz speziell ein Liebesgruß an „meine“ Miso die ich inständig liebe und bei der ich mit Streicheln fast immer gute Werte bekomme!!

Fachübergreifende Diskussionen, Kaffee, Ratschläge, Kuchen, **Silke**, Tränen, Kooperationen, Gespräche, Gossip, Lachen, Trost, **Erna**, Kochstunden, Zittern, alles war da im unglaublichsten Bürotrakt der Welt der das Arbeiten manchmal so leicht und angenehm machte und sicherlich - Bürokraten aufgehört – zu manch Publikationsflut in den letzten 11 Jahren im „SFB-Trakt“ führte weil man gemeinsam stark ist. Aber: Wenn man auseinandergerissen wird sinkt auch der „Hirsch“ und der „Impaktfaktor“ !!!! Persönlich erwähnen möchte ich aber **Cosima, Heidi, Wendy, David** sowie **Anja, Ines, Juliane, Julie, Karen, Naemi**, und **Tom** die unsere Arbeitsgruppe als Doktoranden und Diplomanden verstärkt haben und sowohl im Gelände, im Labor, bei Festen und als Diskussionspartner „Motivationskugeln“ waren. Danke aber auch an die „Zukünftigen“! Ohne euch, **Julie** und **Steffen**, hätte ich den innere Schweinhund hierfür nicht überwunden!

Natürlich auch ein Dank an die Abteilung **MuHS** und **Frauke** sowie den **FB4** die mir den „Umstieg“ zum „Neueinstieg“ möglich und leicht gemacht haben.

Very special thanks go to my friend **Cristina Millan** who read the whole thesis during the „basalt drilling“ on Exp. 344. Thanks for your criticism and you know as a „honey butcher“ I normally “don't give a shit” :-) ……..

Und zum Schluss natürlich den größten Dank an meine Familie, mit **Elke, Ann-Cathrin, Sebastian, Jonas** und **Lea**, die mich immer getragen hat während dieser Zeit und meine Abwesenheit immer ertragen hat und mich trotzdem noch kennt ....

Appendix

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